

AMERICAN CHEMICAL SOCIETY

TABLE OF ATOMIC WEIGHTS OF THE CHEMICAL ELEMENTS 1929

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	Sym- bol	At. Num- ber	At. Weight		Sym- bol	At. Num- ber	At. Weight
Aluminium . . .	Al	13	26.97	Molybdenum . .	Mo	42	96.0
Antimony . . .	Sb	51	121.77	Neodymium . . .	Nd	60	144.27
Argon	A	18	39.94	Neon	Ne	10	20.183
Arsenic	As	33	74.96	Nickel	Ni	28	58.69
Barium	Ba	56	137.36	Nitrogen	N	7	14.008
Beryllium . . .	Be	4	9.02	Osmium	Os	76	190.8
Bismuth	Bi	83	209.00	Oxygen	O	8	16.000
Boron	B	5	10.82	Palladium	Pd	46	106.7
Bromine	Br	35	79.916	Phosphorus . . .	P	15	31.02
Cadmium	Cd	48	112.41	Platinum	Pt	78	195.23
Calcium	Ca	20	40.07	Potassium	K	19	39.10
Carbon	C	6	12.000	Praseodymium . .	Pr	59	140.92
Cerium	Ce	58	140.13	Radium	Ra	88	225.97
Cesium	Cs	55	132.81	Radon (Niton) . .	Rn	86	222
Chlorine	Cl	17	35.457	Rhenium	Re	75	188.7
Chromium	Cr	24	52.01	Rhodium	Rh	45	102.91
Cobalt	Co	27	58.94	Rubidium	Rb	37	85.44
Columbium . . .	Cb	41	93.1	Ruthenium	Ru	44	101.7
Copper	Cu	29	63.57	Samarium	Sm	62	150.43
Dysprosium . . .	Dy	66	162.46	Scandium	Sc	21	45.10
Erbium	Er	68	167.64	Selenium	Se	34	79.2
Europium	Eu	63	152.0	Silicon	Si	14	28.06
Fluorine	F	9	19.00	Silver	Ag	47	107.880
Gadolinium . . .	Gd	64	157.26	Sodium	Na	11	22.997
Gallium	Ga	31	69.72	Strontium	Sr	38	87.63
Germanium . . .	Ge	32	72.60	Sulfur	S	16	32.06
Gold	Au	79	197.2	Tantalum	Ta	73	181.5
Hafnium	Hf	72	178.6	Tellurium	Te	52	127.5
Helium	He	2	4.002	Terbium	Tb	65	159.2
Holmium	Ho	67	163.5	Thallium	Tl	81	204.39
Hydrogen	H	1	1.0078	Thorium	Th	90	232.12
Indium	In	49	114.8	Thulium	Tm	69	169.4
Iodine	I	53	126.932	Tin	Sn	50	118.70
Iridium	Ir	77	193.1	Titanium	Ti	22	47.9
Iron	Fe	26	55.84	Tungsten	W	74	184.0
Krypton	Kr	36	82.9	Uranium	U	92	238.14
Lanthanum . . .	La	57	138.90	Vanadium	V	23	50.96
Lead	Pb	82	207.22	Xenon	Xe	54	130.2
Lithium	Li	3	6.940	Ytterbium	Yb	70	173.6
Lutecium	Lu	71	175.0	Yttrium	Y	39	88.92
Magnesium . . .	Mg	12	24.32	Zinc	Zn	30	65.38
Manganese	Mn	25	54.93	Zirconium	Zr	40	91.22
Mercury	Hg	80	200.61				

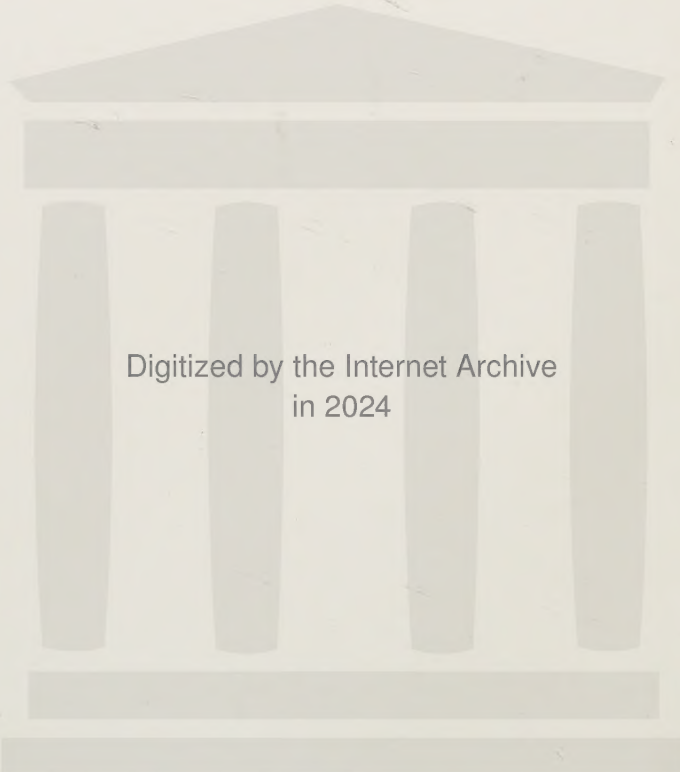
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ROBERT BOYLE (1626-1691).

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INORGANIC CHEMISTRY

FOR COLLEGES

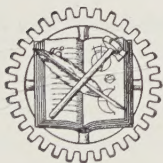
*A Textbook for Students of Second Year
Chemistry*

BY

WILLIAM FOSTER, PH.D.

Professor of Chemistry in Princeton University

THIRD PRINTING



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PREFACE

It is the opinion of educators and of experienced teachers that students who have completed a preparatory course in chemistry should not be taught in classes with beginners when continuing the study of the subject in higher institutions of learning. Since some institutions have limited facilities for instruction, it is not always possible sharply to divide students into two classes; but many colleges and universities are now able to offer a more advanced course as well as an introductory course in general chemistry.

It also is the opinion of teachers of chemistry that those who have completed a high-school course in the subject should not repeat the work of the secondary schools, but it should form the basis for a broader and more thorough course.

To arouse and keep alive the interest of the student in his second-year course, it is desirable to have textbooks in which the order of the subject matter differs somewhat from that in books designed for beginners, or for classes composed of beginners and of those who have studied chemistry in high school. Moreover, the books should be more thorough as well as more difficult.

To meet the needs at Princeton we are offering an "Introductory Course in General Chemistry" and also a course entitled "Advanced General Chemistry and Elementary Qualitative Analysis." The latter course is open to those who have passed chemistry for entrance to the university. It consists of lectures and recitations on the fundamental laws and theories of chemistry and on the elements and their compounds. The laboratory work (one three-hour period weekly) consists of a few fundamental experiments in general chemistry, followed by elementary qualitative analysis. During the first term opportunity is given for the performance of additional experiments by those who elect to do two three-hour periods of laboratory work the second term, which is devoted entirely to qualitative analysis. Students completing this course satisfactorily are permitted to elect organic chemistry or physical chemistry the following year.

The textbook entitled *Inorganic Chemistry for Colleges* is designed for students pursuing a course such as the one outlined above, or for those who have completed a good high-school course in general chemistry.

Having had long experience in teaching chemistry to beginners and also to those who have offered chemistry for entrance to college, as well as much experience on the College Entrance Examination Board, the author believes that he is familiar enough with the actual situation to write a textbook to meet the special need.

The book is divided into four parts, namely:

Part I. — Introductory.

Part II. — The Non-metals.

Part III. — The Metals.

Part IV. — Supplementary: Carbon Compounds.

After certain fundamentals are treated, such as the laws of chemical combination, the atomic theory, formulae, equations, the laws of gases, the kinetic theory, and the internal structure of crystals, the radioactive elements are studied in some detail (Chap. IV) in order to lay an experimental foundation for the study of atomic structure, which is considered in connection with the classification of the elements.

This is one important respect in which the book differs from other textbooks designed for those who have had a preparatory course in chemistry. It seems to the writer that it is logical to study radioactivity before taking up atomic structure and atomic numbers. Many writers, however, postpone the treatment of the radioactive elements until the metals are studied. Indeed, some reserve radioactive substances for the last chapter in the textbook.

The early introduction of radioactivity and of atomic structure gives the student a new view-point and also makes it possible to treat valence, the oxidation-reduction reaction, etc., from the modern standpoint. It should, therefore, arouse the interest of the student.

Since the textbook presupposes an elementary knowledge of certain families of elements (*e.g.*, the halogens and the alkali metals), the early introduction of the classification of the elements needs no defense.

It also is logical to study solution after water is studied, followed by the consideration of atomic and molecular weights, including the freezing point method for the determination of the latter. The treatment of energy and of equilibrium lays a solid foundation for the study of ionization, solubility-product, the oxidation-reduction reaction, etc.

While carbon and a few simple carbon compounds are treated in Part II, organic chemistry proper is reserved for Part IV. This arrangement appears to be best, for many teachers have very little time to devote to the study of carbon compounds. If teachers so desire, however, Part IV, or any portion of it, may be presented in connection with carbon. Probably some teachers will prefer to take up the hydrocarbons and flame after carbon, and there is no reason why this should not be done, if time be available. Part IV is intended to be merely introductory to the study of organic chemistry.

At the conclusion of the chapter on silicon and boron, the non-metals as a whole are briefly reviewed and the more common acids are divided into groups according to the scheme of qualitative analysis.

Part II closes with a chapter on colloids.

Part III is devoted to the metals, the periodic classification being closely followed. As a rule, the general characteristics of a family are given. Not only are the metals of a family discussed with reference to each other, but their relationships to other metals receive attention, thus giving a very broad knowledge.

Parts I-III contain in considerable detail much information needed in the study of analytical chemistry, especially qualitative analysis.

While the theories and laws of chemistry have received fairly full treatment, an endeavor has been made not to neglect the descriptive side of chemistry, nor the innumerable applications of the science.

It is felt that the textbook is well-planned from the standpoint of the student as well as the teacher. The sections are numbered so as to make it easy to refer from section to section. Each chapter is followed by a list of questions, so framed as to test the student's knowledge of the subject matter and also his ability to

reason. Furthermore, there are classified problems in the back part of the book, followed by an appendix which gives much valuable and necessary information.

The author is very grateful to the following colleagues who have been good enough to offer helpful suggestions and criticisms: Professors Hugh Stott Taylor, Charles P. Smyth, N. H. Furman, and Francis B. Stewart. Also to Mr. John H. Wallace, Jr., who read both the manuscript and the proof.

The author also is indebted to the Princeton University Press and to The Century Company for permission freely to use material from his books entitled, respectively, *Introduction to General Chemistry* and *The Romance of Chemistry*. For many illustrations, charts, and drawings the author is under deep obligation to various individuals and to many industrial firms.

WILLIAM FOSTER

PRINCETON, N. J., February 1929.

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PART I
INTRODUCTORY

HISTORICAL INTRODUCTION

When we attempt to find the meaning of the word "Chemistry," we are carried back to the most ancient peoples — to the very beginning of civilization. Scholars are not in agreement as to its meaning. Some hold that the word refers to the land of Chemi (Egypt), which was the cradle of chemistry; while others believe it to have been derived from a Greek word meaning a mingling or an infusion, for chemistry was at first the art of extracting the juices from plants for medicinal purposes. It is said, therefore, that chemistry originated in the temples where priests experimented in preparing medicines.

Egypt was overrun by the Arabians about the middle of the 7th century. The invaders learned something about chemistry from the Egyptians, and they prefixed the Arabic article *al* to the word *chemia*; hence the word "Alchemy." The aim of this imaginary art was to transmute the baser metals into silver and gold, and to find the panacea, or universal remedy for disease. Alchemy led the way to modern chemistry.

The Egyptians, the Phoenicians, the Jews, and other ancient peoples possessed some knowledge of chemical processes, which were developed largely by accident and were applied for their practical results. Indeed, a practical knowledge of certain chemical operations must have antedated the dawn of history. Ancient records and the result of excavations show that the Egyptians were acquainted with the working of gold, silver, copper, and iron; that they understood the art of manufacturing vessels of glass, and pottery from clay; knew how to produce enamels, alloys, and artificial gems; greatly developed the arts of dyeing and of embalming their dead, and prepared many medicines, paints, and other products. Inscriptions representing glass-makers plying their art have been unearthed in Egyptian monuments of the 11th dynasty, showing that considerable skill in glass-making was developed at least 2,000 years before the Christian era. Glass beads have been found in mummy cases at least 3,000 years old, and glass articles have been discovered in the excavations of Nineveh.

The ancients used indigo, in dyeing, hundreds of years before

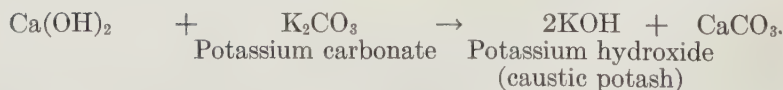
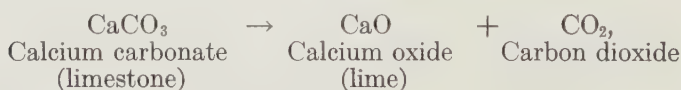
our era; and they were also familiar with vinegar, salt, wine, and other products.

There is evidence that the Egyptians employed paints for the decoration of their tombs as early as 2,500 B.C. The Assyrians, the Greeks, and the Romans also practised the decorative art. The color pigments discovered at Pompeii and Herculaneum are of much interest, for they were liberally applied in the decoration of buildings and other structures. The colors used were largely earth colors, such as yellow ochers, the red oxide of iron, naturally occurring vermilion, and copper-bearing minerals. Pompeian red, for example, is famous. Chemicals have been employed as cosmetics for thousands of years; the women in the East have long used antimony trisulfide for painting the eyebrows. (See 2 Kings IX. 30, and Ezekiel XXIII. 40.)

The Hindus, more than 2,000 years ago, knew how to produce caustic potash (KOH) from potassium carbonate (K_2CO_3) obtained by burning plants or wood. The process is given in the *Susruta*, an old Hindu work, and is described as follows:

“Collect several kinds of limestone and shells and burn them strongly and add water to the resulting product. Next mix this slaked lime with the lixiviated liquid obtained above, *i.e.*, by treating ashes of wood with water and boil and stir with an iron ladle.”

The reactions taking place in this process are represented in the modern way by the following equations:



This method did not appear in any European treatise before the 16th or the 17th century.

The Hindus, at a very early date, also attained a high degree of skill in metallurgy. This is well illustrated in the celebrated iron pillar near Delhi, which was manufactured of pure malleable metal about 1,500 years ago. This pillar weighs 55 tons, and is

still standing and unruined, and the inscription on it is as clear and sharp now as it was when the pillar was erected.

While the ancient world possessed certain facts in the field of chemistry, experimental investigation was almost unknown. At that time the leading scholars were fond of speculation, and thought it beneath their dignity to experiment with gross matter. There was a vast amount of speculation by philosophers as to the nature of things, but the hypotheses advanced to explain occurrences or phenomena were often fanciful and extravagant. Beyond or above the material world there were certain philosophical principles such as the divine spirit or essence which pervaded all matter.

In the narrow sense of the term, alchemy is the pretended art of transmuting the base metals into the noble metals — silver and gold. From early records it appears that the idea of transmutation arose in the Greek colony of Alexandria, Egypt, the “Queen City of the Mediterranean,” where astronomy and mathematics were greatly developed. In this ancient city, where alchemy had its beginning, the Greek philosophy — the teachings of Plato and of Aristotle — was predominant. The so-called doctrine of Empedocles (about 450 B.C.) and Aristotle of the four elements — Earth, Water, Air, and Fire — signified that matter had certain characteristics and fundamental properties. Thus, “earth” implied the properties of cold and dryness; “water,” cold and moisture; “air,” heat and moisture; and “fire,” heat and dryness. Presumably all matter was of one kind, and the wide variety of matter was thought to be due to the greater or less abundance of these four elements or principles.

The ancients believed that there was a fundamental kind of matter which entered into the composition of all forms of matter; this they termed **hyle** (Greek, meaning *matter*). “Matter is one,” was a basic proposition of Plato’s. The early philosophers also held that all nature is striving toward improvement. From such ideas one would conclude that all metals are alike in substance; that there is no essential difference between copper and gold. It was believed that material things were capable of infinite change; and it was known that metals, on exposure to the agencies of heat, air, and moisture, underwent certain changes, such as rusting. These changes naturally suggested the idea of transmutation. Metals were supposed to possess different degrees of purity, and it was believed that by subjecting them to fire and other agencies it was possible to pass step by step from the

base metals to the noble metals — silver and gold — the only perfect ones. The alchemists obtained lead from galena, or lead sulfide, and silver from the lead; but they did not realize that silver is often associated with lead. It is not so strange that they thought they should be able to make gold.

According to Gibbon, the historian, the persecution by Diocletian is the first authentic event in the history of alchemy. About A.D. 290 he caused an inquiry to be made "for all the ancient books which treated of the admirable art of making gold and silver, and without pity committed them to the flames, apprehensive, as we are assured, lest the opulence of the Egyptians should inspire them with confidence against the empire."

In the Leyden museum there are several papyri which were discovered in Thebes, and were perhaps written in the third century of our era. One of these gives a number of recipes, written in Greek, for the treatment of base metals to form products resembling gold, which were to be used in the manufacture of imitation jewelry. The oldest works of a strictly chemical character date, therefore, from the third century.

We are told that "the germs of chemical knowledge which had lain hidden in the brains of a few philosophers, attained to a marvelous growth among the Arabians." Geber, as he became known to the Western nations, was the most celebrated alchemist among them.

The Arabians carried alchemy into Spain, from which country it spread over western Europe.

As so well expressed by Gibbon: "The conquest of Egypt by the Arabs diffused that vain science over the globe. Congenial to the avarice of the human heart, it was studied in China and in Europe, with equal eagerness, and with equal success. The darkness of the Middle Ages insured a favorable reception to every tale of wonder, and the revival of learning gave new vigor to hope and suggested more specious arts of deception."

In the 14th century the study of alchemy extended throughout the civilized world. While transmutation was the leading idea of alchemists for a thousand years, alchemy was more than a vain thirst for silver and gold; in its broader meaning it stands for the chemistry of the Middle Ages. According to Liebig, alchemy was "never at any time anything different from chemistry." Alchemy as practised during the Middle Ages was the logical outgrowth of the philosophical thinking of the ancient Greeks.

It should be added that the ancients thought the transmuta-

tion of the metals could be brought about by means of the *philosopher's stone*, which was mentioned in their writings as a red powder with a peculiar odor. It was called the *grand elixir*, or the *magisterium* (masterpiece); and it was believed by such eminent men as Roger Bacon, who lived in the 13th century, to possess the power of prolonging life and of healing disease. Bacon was a man of remarkable ability and intellectual curiosity. He may be regarded as the originator of experimental research, for he carefully planned experiments to test various theories. According to Bacon, "gold is the most perfect of metals because in it Nature has finished her work."

The alchemists graded metals according to color; the base metals possessed little color and were readily tarnished. They placed the yellow color of gold above the pale white of silver; indeed, gold was supposed to reflect the yellow or red firelight of the sun, the color of which never changed, while silver reflected the soft white light of the moon; but as the light of silver was paler, the metal was capable of taking on a bronze color.

Even before the Christian era, an industry which may be termed *imitation* had arisen throughout the Mediterranean countries. Thus, imitation pearls were produced from secretions found in bamboo; and an excellent imitation of royal or Tyrian purple (which was obtained from a snail-like shell-fish of the Mediterranean, and was very expensive) was secured from plants. Certain alloys which resembled silver and gold were also produced. The alchemists "made the discovery that certain colors, some very beautiful, were produced upon the surface of the alloys thus prepared and that these colors could be varied by the use of different fluxes, just as the colors of fabrics depended on the mordants used." According to A. J. Hopkins, the medieval alchemist was primarily interested in color-effect and decoration. He holds that real alchemy did not last more than a few centuries after the persecution by Diocletian, and terms the writers and adepts in alchemy, about the 13th century, pseudo-alchemists.

In the 16th century, chemistry strove to free itself from the domination of the alchemistic idea, and the era of Medical Chemistry, or the Iatrochemical (Greek *ιατρῶς*, *physician*) period, began. Chemistry was regarded as the handmaid of medicine, and many valuable medicines were discovered. The great precursor of the Medical Chemists was the renowned Paracelsus, who was born in Switzerland in 1493, and was the son of a physician. He gave a new direction to alchemy by declaring that "the

object of chemistry is not to make gold but to prepare medicines"; and this union of chemistry with medicine was a dominant characteristic of the Iatrochemical School.

Paracelsus declared that the human body consisted of sulfur, mercury, and common salt, and that the health of the body depended upon the presence of the proper amount of these substances; when any of these ingredients changed, illness resulted, and it could be cured only by the administration of chemical medicines. He was familiar with the works of magicians and alchemists, and traveled long distances on foot, collecting a variety of information regarding the art of healing, from wise men and women, barbers, blacksmiths, and others. He also spent much time in the mines of the Tyrol. After many strange experiences and vicissitudes this remarkable man again resumed his wanderings, and was finally thrown from a window and killed by the servants of a physician in Salzburg, in 1541.

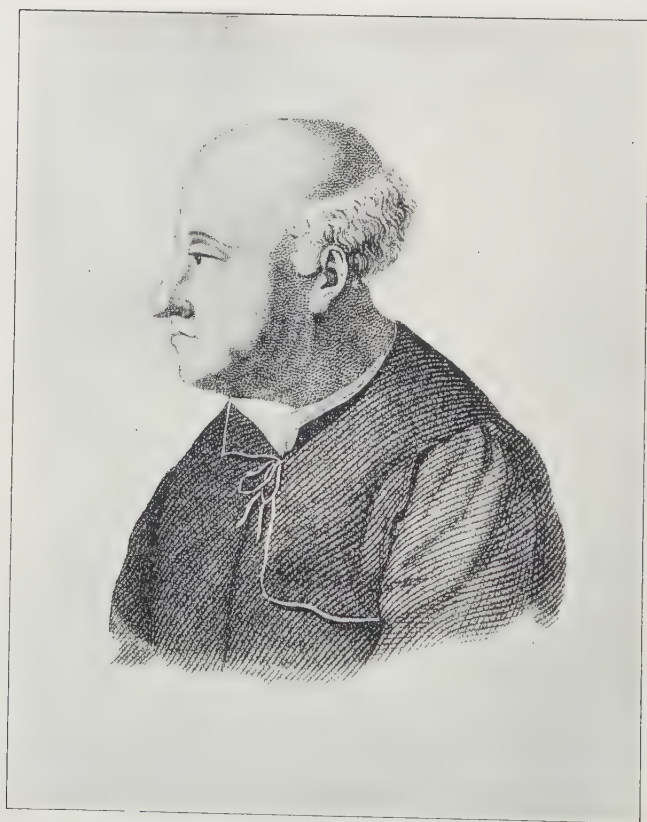
Paracelsus contributed to medicine many valuable preparations, such as tincture of opium, or laudanum — the name by which it is still known. He was a close observer, and his practice of medicine was based upon careful observation now universally recognized. He used to say that all the accumulations of the medical lore before him were not worth the sole of his boot. His motto was: "Let him not belong to another who may be his own."

Other renowned men of the Iatrochemical period were Georg Agricola, Van Helmont, and Glauber. Agricola was born in Germany in 1490, and became a noted physician. He was therefore a contemporary of Paracelsus, but, unlike the latter, he was not much interested in the storms which raged in the field of medicine at that time. Agricola did pioneer work in metallurgy, or the art of extracting metals from their ores. He was led to devote himself to mineralogy and metallurgy by the flourishing mining and smelting industry of Saxony. His great work on winning metals from their ores, *De Re Metallica*, served as a useful textbook until comparatively recent times.

The era of medical chemistry continued up to the end of the 17th century, when certain views entertained by Paracelsus and others were overthrown by Robert Boyle (1626–1691), a far-seeing philosopher, who was the first real chemist in the scientific sense of the term. Boyle is best known as the author of *The Sceptical Chymist* and as the discoverer of the law which is associated with his name. He was a contemporary of Newton. Boyle, following the method of Roger Bacon, laid great stress on



THE ALCHEMIST.



PARACELSUS (1493-1541)

experimental and inductive methods. "First to doubt, then to enquire, and then to discover, was his method." He also clearly defined an "element" for the first time.

About this time Becher and Stahl of Germany advanced the Phlogiston Theory of combustion. The nature of fire or combustion was a riddle until after the discovery of oxygen by Joseph Priestley, in 1774.

Plato assumed that all combustible bodies or substances contained a common element — inflammable principle — which enabled them to burn. This explanation of combustion was quite generally accepted until the 18th century. Some scholars thought that the inflammable principle was sulfur; hence the saying, "Where there are fire and heat, there is sulfur."

Johann Becher in 1669 pointed out that there are many combustible materials which do not contain sulfur; and he postulated a principle termed by him *terra pinguis*, meaning fatty or inflammable earth. Subsequently Georg Ernst Stahl, who was a professor at Halle and a good chemist and successful teacher, developed Becher's hypothesis and gave the name **phlogiston** (Greek *φλογιστός*, *set on fire*) to his *terra pinguis*. It is well known to all chemists that Stahl and his followers held that when bodies burned or when metals were calcined, a sort of fire-stuff (*phlogiston*) escaped. Nobody seemed to have a very definite notion as to the real nature of phlogiston. Some thought that sulfur and soot were nearly pure phlogiston; others, that phlogiston was immaterial, or light, or hydrogen. The principle was supposed to be united with combustible bodies and to be separated from incombustible bodies.

The phlogiston theory became thoroughly entrenched in the 18th century, being advocated by all the leading chemists.

The discovery and investigation of gases, such as oxygen, nitrogen, hydrogen, and carbon dioxide, played a great part in shaping chemistry. Many gases were discovered by Joseph Priestley and by K. W. Scheele, and their properties excited the chemical world. Improved methods for collecting, handling, and studying gases were devised, Priestley being the first to describe their collection over mercury. After the discovery of oxygen, a new era dawned in the history of chemistry; for the brilliant and versatile Lavoisier proved that combustion is the rapid chemical union of a substance with oxygen, accompanied by the evolution of heat and light. Joseph Black showed the precise difference between carbon dioxide and air, and Henry Cavendish established

the elementary nature of hydrogen, and proved that it burns in air or oxygen to form water.

The chemical balance became an important instrument in the hands of the chemist in the latter part of the 18th century, and Lavoisier demonstrated the supreme importance of the proportions by weight in chemical change.

About the beginning of the 19th century, John Dalton (1766–1844) propounded his atomic hypothesis, which assumed that chemical elements consisted of ultimate particles not further divisible — of atoms. The atomic hypothesis has had a supreme influence in the development of chemistry.

Berzelius (1779–1848), the great Swedish chemist, said: “the hypothesis of Dalton, if firmly supported by facts, would be the greatest advance chemistry has yet made toward its perfection as a science.”

The gradual recognition of the laws of Definite and Multiple Proportions, which are so closely connected with the atomic hypothesis, formed the basis of modern theoretical chemistry. Berzelius, one of the greatest masters in analytical chemistry, subjected these laws to a very rigid test and placed them on a firm foundation. He prepared a table of accurate atomic weights, and was the author of the system of chemical symbols.

Since the introduction of the experimental method in the study of the science, progress has been steady and rapid. The advance which has been made in the domain of chemistry since the discovery of oxygen and the establishment of the laws of chemical combination has been remarkable.

In the study of chemistry it is well to keep in mind the words in which Scheele characterized his own efforts: “It is the truth alone we desire to know, and what joy there is in discovering it.”

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CHAPTER I

TERMINOLOGY. CHANGES IN MATTER. COMBINATION BY WEIGHT

Chemistry, like the other sciences, has a terminology of its own. As the natural sciences are related, some of the scientific terms are used in common. It is important for the student to become familiar with them at the very outset so that they may be used readily, intelligently, and accurately.

SOME CHEMICAL TERMS

1. **Matter.** — Matter may be defined as anything which possesses weight or mass. Matter occupies space and may be perceived ordinarily by the sense of touch.

Chemistry deals with all kinds of matter — simple and complex, natural and artificial or manufactured.

Matter exists in three different states, the **solid**, the **liquid**, and the **gaseous** states. These states of matter depend upon temperature and pressure. Thus, water exists as ice, liquid, and vapor. At 0° C., liquid water freezes, or ice melts to form a liquid; 0° C. is therefore the fusion point of ice, or its melting point. If heat is supplied to water at 100° C., under 760 mm. of pressure, it boils, *i.e.*, gives off vapor (steam) freely.

Carbon dioxide, oxygen, chlorine, zinc, mercury, alcohol, and many other kinds of matter may also be prepared or obtained in the three different states of aggregation.

In general, solids have a greater density, *i.e.*, weigh more per unit volume, than do liquids, while the latter are denser than gases.

2. **Properties.** — The different kinds of matter have qualities known as *properties*. When the chemist examines a specimen of ordinary sulfur, he finds that it has a pale-yellow color, that its density is 2.06 (it therefore sinks in water), it melts at 112.8° C., boils at 444.7° C., is insoluble in water, very soluble in carbon disulfide, a non-conductor of electricity, etc. These qualities of sulfur are often called the **specific properties** of this particular

kind of matter, because they are characteristic. The properties enumerated are called specific physical properties. When sulfur is heated in the air, however, it burns, forming the gas sulfur dioxide, which possesses a sharp odor. This involves the transformation of the sulfur into another substance having totally different properties; hence the change is known as a chemical change, and sulfur has the chemical property of burning when heated in the air or oxygen.

Carbon (the diamond, graphite, and charcoal) has properties very different from those of sulfur, and water and alcohol each has its own characteristic properties.

The properties of each kind of matter are used in the identification or recognition of the material.

In the recognition of materials, it is not necessary to examine all of their properties. The chemist is guided by the following principle, as stated by Ostwald:

“When two substances agree entirely in some few properties, they agree also with regard to all other properties.”

Pure water, for example, is odorless, tasteless, and colorless when viewed in thin layers; it boils at 100°C ., the pressure being one standard atmosphere, freezes at 0°C ., and leaves no residue when evaporated to dryness. No other known substance possesses all these properties; therefore, when we examine a substance and find that it has these properties, we can confidently conclude it is water. This principle of Ostwald enables the chemist to recognize substances with certainty after testing only a few of their properties; analysis is therefore much simplified.

3. Substance and Bodies. — A **substance** is a particular species of matter possessing definite properties. Thus, gold, iron, water, salt, etc., are substances. In thinking of substances, we leave size and form out of account. A substance is identified by its properties.

A **body** or **specimen** is any portion of matter having a definite spacial limit or form. Gold is a substance of which various bodies or objects are made.

Bodies are either **homogeneous** or **heterogeneous**. When a specimen of a pure substance, such as gold or alcohol, is examined, it is found to possess identical properties throughout. Such a body consists of only one material or phase; it is therefore homogeneous.

When old-fashioned gunpowder and granite are examined, it is found that they consist of more than one ingredient. Thus,

in granite there are three different minerals, namely, quartz (hard enough to scratch glass), feldspar (pink), and mica (can be split into very thin leaves). When granite is crushed, these three minerals drop apart. Granite is therefore a heterogeneous body, for it consists of more than one visible component lying side by side.

The crystalline forms of the components of granite are shown in Fig. 1. *A* represents a crystal of quartz; *B*, feldspar; and *C*, mica. The forms are very different.

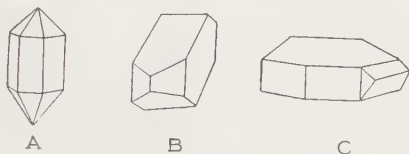


FIG. 1.

Heterogeneous bodies, or mixtures, can be separated into their component ingredients by purely mechanical means. Thus, when flour is examined under the microscope, granules of starch may be seen, along with other matter. It may be separated into its chief components — starch and gluten — as follows:

A small quantity of flour is placed in a cheese-cloth bag which is then closed with a string. By kneading the bag under water, the liquid becomes milky owing to granules of starch which pass through the cloth. The water is changed frequently and the kneading continued; a sticky material — gluten — is left in the bag.

The ingredients of a heterogeneous body, such as granite or gunpowder, are termed **phases**. The concept phase has been defined as follows:¹ “*A phase is any part of a system, which is homogeneous throughout, it is bounded by a surface and is mechanically separable from the other parts of the system.*”

4. Law of Component Substances. — In 1742, Lomonossov, a Russian author, statesman, and chemist, enunciated the above-named law. It may be stated as follows:

“**Every material is composed of one substance, or is a mixture of two or more component substances, each of which has a definite set of specific physical properties.**”

5. Solutions. — When a sugar solution is examined with and without the aid of a microscope, it is found to be homogeneous. It is impossible to remove the sugar from the water by means of a filter. Is a sugar solution, then, a pure substance? While such a solution has the appearance of a pure substance, it is not really so. The properties, *e.g.*, density and sweetness, may be varied by dis-

¹ Taylor, *Elementary Physical Chemistry*, p. 311.

solving more or less sugar in a given quantity of water. The properties of a pure substance are always the same under the same conditions. Water, for example, has a density of 1 at 4° C., while the density of a sugar solution can be varied by changing the concentration of the solution. Water boils at 100° C., under standard atmospheric pressure, while the boiling point of a sugar solution increases with concentration. *In general, pure substances have specific physical properties, under given conditions of temperature and pressure, while the properties of solutions depend upon their composition as well.*

Solutions are not restricted to any particular state of matter.

Gases which do not interact chemically are mutually soluble, that is, pass into a homogeneous condition; therefore, there can be only a single gaseous phase in any system made up of gases, such as a mixture of nitrogen and oxygen (the atmosphere).

6. Mixtures. — From our study of heterogeneous bodies (3), we have seen that a mixture contains two or more distinct ingredients or components. The components of a mixture retain their properties as if each were there alone. For example, when iron and sulfur are rubbed together in a mortar, the two substances form a mixture. The components are visible under a lens. Moreover, the iron may be separated from the sulfur by means of a magnet, and the sulfur is readily soluble in carbon disulfide (very inflammable!).

Ordinary concrete is a mixture of crushed stone, sand, and cement; gunpowder, a mixture of potassium nitrate (saltpeter or niter), sulfur, and charcoal.

It should be noted that *the composition of a mixture is not definite or constant*, for it may be changed at will by adding more or less of the different components.

When small quantities of foreign matter are contained in the main portion of a specimen of matter, they are called *impurities*: e.g., common salt contains magnesium chloride as an impurity. This explains the fact that salt becomes moist during hot, wet weather. Natural waters always contain in solution certain impurities. Solids may be recovered from water by evaporation to dryness. In order to purify water, it is carefully distilled. The preparation of a pure substance is often attended by numerous difficulties.

7. Components. — The separate ingredients of a mixture are called components (Latin, *put with*). The components are put together without a change in their nature or properties, and they

may also be separated without changing their properties, *e.g.*, by mechanical means.

CHANGES IN MATTER

8. Physical Changes. — Changes often take place in matter which do not involve the transformation of the matter into a new substance or substances having a new set of properties. These changes are called physical changes. Such changes are well illustrated in the freezing of water, the formation of dew, the crushing of stone, the heating of platinum, the magnetization of iron, and the melting of solids such as gold and ice.

None of these changes involves the transformation of the substance into a new substance possessing totally different properties. Changes of this variety are matters of everyday experience.

In many cases, physical changes are temporary or transient in nature, and are not deep-seated, as is the case, for example, when carbon or sulfur is burned.

9. Chemical Changes. — There are many changes which involve the transformation of matter into another substance or substances possessing specific properties different from those of the original matter. Such changes are known as chemical changes.

We are all familiar with the corrosion of metals, the combustion of fuel, the decay of animal and of vegetable matter, the souring of milk, the fermentation of sweet cider to form an alcoholic liquid, and of the transformation of cider into vinegar. The idea of chemical change is well expressed in the following words of Sir Humphry Davy: "Most of the substances belonging to our globe are constantly undergoing alterations in sensible qualities, and one variety becomes, as it were, transformed into another. Such changes, whether natural or artificial, slowly or rapidly performed, are called chemical."

VARIETIES OF CHEMICAL CHANGE

10. Combination. — Magnesium, as is well known, burns in oxygen to form magnesium oxide. In this reaction two substances, *A* and *B*, combine to form a third substance, *C*:



At the outset it is important to learn that chemical combination takes place between definite weights of substance to form a defi-

nite weight of the product (see Sec. 26). By burning a known weight of magnesium in a crucible and then weighing the oxide formed, chemists have found that 1 part by weight of magnesium combines with 0.66 part of oxygen to form 1.66 parts of the oxide. If we use the gram as the unit of weight, the condensed statement reads as follows:

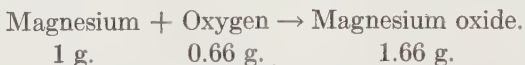


FIG. 2.

Another Illustration of Combination: Iron and Sulfur. Iron filings and sulfur have very different properties (2). Iron is magnetic and dissolves in dilute hydrochloric acid, forming hydrogen (a colorless gas) and ferrous chloride. Sulfur is not magnetic and is insoluble in dilute hydrochloric acid, but readily soluble in the liquid carbon disulfide, in which iron is insoluble. Sulfur also has a definite crystalline form (Fig. 2).

When iron filings and sulfur are thoroughly ground together in a mortar, a greenish-black powder is obtained, which differs in appearance from either of the components. When the powder

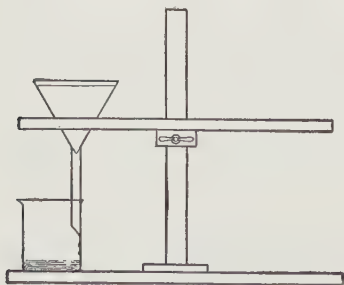


FIG. 3.

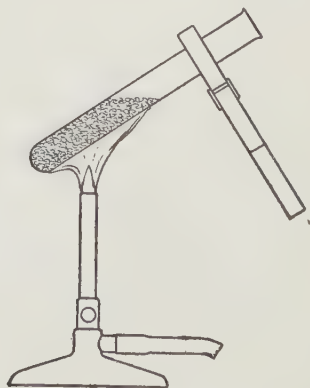
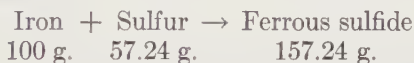


FIG. 4.

is tested, however, the iron and the sulfur are found to be present as such. Thus, the former is attracted by a magnet, and it dissolves in hydrochloric acid, leaving sulfur (yellow). When a portion of the powder is shaken in a test-tube with carbon disulfide and the contents of the tube poured into a folded filter

(Fig. 3), iron is left on the filter. By allowing the liquid to evaporate in a dish [hood], sulfur is obtained, showing that we are dealing with a heterogeneous mixture (3).

When another portion of the original mixture is heated in a test-tube until the mass glows, a very deep-seated change may be observed to take place (Fig. 4). When the test-tube is allowed to cool and the material in it examined, it is found to be black, porous, non-magnetic, and insoluble in carbon disulfide. Close examination with a lens or a microscope does not reveal the presence of either iron or sulfur. When a portion of the solid is treated with dilute hydrochloric acid, hydrogen sulfide, a gas possessing a disagreeable odor, is evolved. The product formed is known as ferrous sulfide:



How many grams of iron would be required to unite with 32 g. of sulfur to form ferrous sulfide, and what weight of the last substance would be obtained?

When two or more distinct substances unite to form one new substance, an act of chemical combination is said to have occurred.

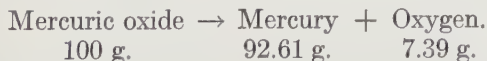
11. Decomposition. — When red oxide of mercury (mercuric oxide) is heated in a test-tube, a gas is liberated which causes a glowing splinter to burst into flame. The colorless gas formed is a good supporter of combustion; it is oxygen. During the heating a shining mirror forms on the sides of the tube, and in the course of a few minutes the bright substance appears as globules. It is readily recognized as the metal mercury, or quicksilver.

The breaking down of mercuric oxide into mercury and oxygen is known as decomposition. In general, we have:



The single substance, *A*, splits into two substances, *B* and *C*. Certain substances may be decomposed into more than two substances.

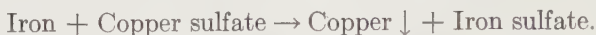
The condensed statement for the decomposition of mercuric oxide may be written thus:



How many grams of mercuric oxide would be required to prepare 16 g. of oxygen? How many grams of mercury are required to unite with 16 g. of oxygen to form mercuric oxide?

Note that decomposition is the reverse of combination, and is a second variety of chemical change.

12. Displacement. — A third variety of chemical change is known as displacement. This variety of change may be readily illustrated by dipping a bright steel knife or spatula into an aqueous solution of copper sulfate (blue vitriol). The spatula is soon coated with the red metal copper, some of the iron going into solution to displace the copper:



In the case of displacement, one simple substance interacts with one compound substance to form one simple substance and one compound substance.

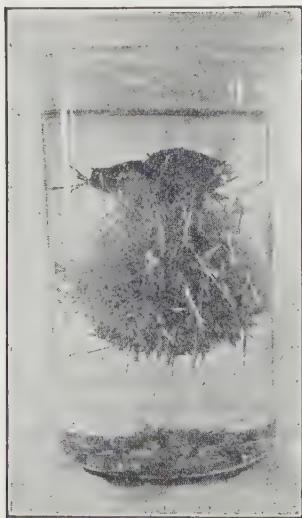
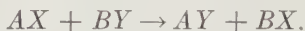


FIG. 5.

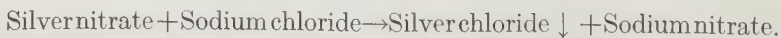
Displacement also may be illustrated by enclosing a small amount of mercury in a porous bag and suspending it in a solution of silver nitrate (Fig. 5), or by suspending a rod of zinc in a solution of a lead salt.

13. Double Decomposition. — A fourth variety of chemical change, called double decomposition, is very common. In this case, *two compound substances interact to form two other compound substances:*



This kind of change may be illustrated by mixing aqueous solutions of silver nitrate and sodium chloride (common salt). A white curdy precipitate of silver chloride (in-

soluble in water) is obtained. Silver nitrate and sodium chloride decompose, and the parts into which they split unite to form silver chloride and sodium nitrate:



By filtering off the silver chloride and evaporating the filtrate to dryness, sodium nitrate is obtained. This substance occurs in nature as Chile salt peter, and its crystalline form and other properties are unlike those of sodium chloride. When silver chloride

is exposed to the light, it turns dark, due to slow decomposition into its constituent elements, chlorine and silver. Double decomposition is sometimes called **metathesis**.

14. **Chemical Reactions.** — In studying different varieties of chemical change, we have observed that various substances may be transformed into other substances having different properties. Any chemical change in matter, whether combination, decomposition, displacement, or double decomposition, which involves the transformation of matter into a new substance or substances is termed a **chemical reaction**, or **action**, or **interaction**.

It is of interest to note that transformations in matter are accompanied either by the consumption or the production of energy, such as heat, light, and electricity.

15. **Elements.** — In our study we have seen that magnesium and oxygen unite in definite proportion by weight to form a definite weight of magnesium oxide (10). The weight of the magnesium oxide is exactly equal to the sum of the weights of its two constituents.

We also have seen that iron and sulfur combine in a definite proportion by weight to form the substance ferrous sulfide.

Furthermore, we have seen that mercuric oxide can be decomposed into more "simple" substances, mercury and oxygen; and that a given weight of the oxide yields definite weights of mercury and oxygen. The chemist has not been able to decompose magnesium, oxygen, iron, sulfur, or mercury into simpler substances. It also is true that in decomposing substances found in nature, such as water and salt, one always comes to substances which resist all efforts further to decompose them. These simple forms of matter are termed elements, about ninety of which have been discovered. Thus, water contains the elements hydrogen and oxygen. All the compound substances known to us have been formed by the combination of, or contain in chemical union, the elementary forms of matter.

Robert Boyle, in 1661, was the first scientist clearly to define an element. According to him, "the elements are the practical limits of chemical analysis, or are substances incapable of decomposition by any means with which we are at present acquainted."

In 1789 Lavoisier stated very clearly the difference between elements and compounds. In the time of Lavoisier only twenty-three elements were known.

It should be noted that *the term element may be used in two senses:*

(1) It means one of the simple forms of matter in the *free state*. Thus, we speak of "the element silver," meaning free, elementary silver, or the metal silver.

(2) The word element also means one of the simple forms of matter in *chemical combination*. Thus, we speak of the element silver in silver chloride, iron in ferric oxide (one of the most important ores of iron), etc.

16. **The Definition of Element Provisional.**—While the definition of an element given in the previous section answers for practical purposes at the present time, the student should know that certain substances which were once regarded as elements have been decomposed into simpler substances. Thus, Humphry Davy (1778–1829), early in the 19th century, succeeded in the isolation of such metals as calcium, sodium, and potassium from hitherto undecomposed substances which were regarded as elements. Quicklime, *e.g.*, was regarded as an element until Davy (1807) showed it to be an oxide of calcium.

In recent years scientists have discovered that certain substances known as **radioactive elements** decompose spontaneously into other elements. The chemist has no control over these transformations. Thus, the element radium (a metal belonging to the calcium family) spontaneously splits up, yielding a number of other elements, such as helium, radon, and lead. The reasons for regarding these radioactive substances as elements will be taken up subsequently (Chap. IV).

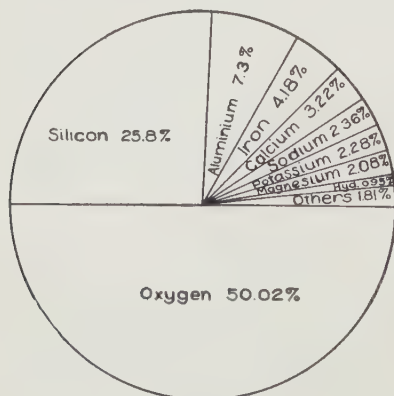


FIG. 6.

17. The Common Elements.

—Of the ninety known elements, only about one-fourth are abundant; and some elements, for example, radium and xenon, are scarce or rare. Only about twenty of the elements occur in nature in the free state. About one-half of the elements are encountered in substances commonly examined in chemical laboratories. Some of the most common and abundant elements are: oxygen, silicon,

aluminium, iron, calcium, sodium, potassium, magnesium, hydrogen, titanium, chlorine, and carbon.

18. **Composition of the Earth's Shell.** — F. W. Clarke has made an estimate of the occurrence of the elements in the solid shell of the earth, the sea and other waters, and in the air.

An examination of Clarke's table given below shows that *twenty elements constitute 99.5 per cent of the earth's crust*. The other sixty-three elements are estimated to constitute 0.5 per cent (Fig. 6).

Oxygen is by far the most abundant of the elements (about 50 per cent), followed by silicon (about 28 per cent). Aluminium is the most abundant metal (nearly 8 per cent), followed by iron (4.5 per cent).

CLARKE'S TABLE

	Solid Shell, 93 Per cent	Ocean 7 Per cent	Average, Including Atmosphere
Oxygen.....	47.33	85.79	50.02
Silicon.....	27.74	25.80
Aluminium.....	7.85	7.30
Iron.....	4.50	4.18
Calcium.....	3.47	0.05	3.22
Magnesium.....	2.24	0.14	2.08
Sodium.....	2.46	1.14	2.36
Potassium.....	2.46	0.04	2.28
Hydrogen.....	0.22	10.67	0.95
Titanium.....	0.46	0.43
Carbon.....	0.19	0.002	0.18
Chlorine.....	0.07	2.07	0.20
Bromine.....	0.008
Phosphorus.....	0.12	0.11
Sulfur.....	0.12	0.09	0.11
Barium.....	0.05	0.08
Manganese.....	0.08	0.08
Strontium.....	0.02	0.02
Nitrogen.....	0.03
Fluorine.....	0.10	0.10
Other elements...	0.50	0.47
	100.00	100.00	100.00

19. **Compound Substances.** — Compounds are pure substances capable of being decomposed into, or formed from, other substances. Thus, mercuric oxide yields mercury and oxygen, when heated.

Compounds are exceedingly numerous, more than 250,000 different ones being known. The known carbon compounds number over 225,000.

The chief characteristics of a compound are that it always con-

tains the same elements in chemical union and they are present in a constant proportion by weight. Pure water, for example, contains 11.19 per cent of hydrogen and 88.81 per cent of oxygen. A compound is also homogeneous.

A mixture, on the other hand, is made up of two or more independent components which are variable in amount. A mixture is heterogeneous, and in many cases it may be readily separated into its components by mechanical means.

20. Constituents. — The term constituent (Latin, *standing together*) refers to the elements present in compounds. Thus, water contains the constituents hydrogen and oxygen; iron rust (ferric oxide), the constituents iron and oxygen. The constituents of a compound may be liberated. When iron oxide is treated in a blast furnace, the metal iron is liberated.

COMBINATION BY WEIGHT

21. Mass and Weight. — A mass is a definite quantity of matter. The mass of a body is constant, *i.e.*, it is independent of its position with respect to other bodies.

The weight of a body depends upon its position in relation to the center of the attracting body (the earth).

$W = Mg$, where W = weight, M = mass, and g the acceleration due to gravity.

Inasmuch as mass and weight are always directly proportional to each other, the two terms may be used interchangeably at any particular place.

The **unit of mass** is the **gram**, which is the thousandth part of the standard mass of metal (an alloy of platinum-iridium) known as a Kilogram. The international prototype kilogram is kept at the International Bureau of Weight and Measures, near Paris.

22. Density. — The ratio of mass to volume of any particular body or material is called its density. In other words, it is the mass per unit volume. It may be expressed by the formula

$$D = \frac{M}{V}, \text{ in which } D = \text{density, } M = \text{mass, and } V = \text{volume.}$$

M is expressed in grams and V in cubic centimeters (cc.). Water at 4° C. has a density of 1. Platinum has a density of 21.4, which means that one cubic centimeter of the metal weighs 21.4 g.

23. The Balance. — The balance is an instrument for determining the relative weights or masses of bodies. By means of the

balance the mass of a given body is compared with the unit of mass. Since mass is proportional to weight, we can measure the one by means of the other. The weight of 1 g. is taken universally as the unit of weight. The multiples and sub-divisions of the gram may be found in the Appendix.

The chemical balance has been of the greatest service in the development of chemistry; for by its use the important laws of chemical combination were discovered.

Lavoisier, during the latter part of the eighteenth century, recognized and laid great stress upon the use of the balance as a trustworthy guide in chemical work. None of the early investigators used the balance as an aid to chemical work with such a definite aim as did Lavoisier.

24. The Law of the Conservation of Mass. — In 1774 Lavoisier heated tin with air in a closed vessel, and he observed that there was no change in the weight of the system notwithstanding the fact that the tin combined with oxygen of the air to form a white powder (stannic oxide). The conclusion arrived at by Lavoisier was stated thus: "Nothing can be created, and in every process there is just as much substance (quantity of matter) present before and after the process has taken place. There is only a change or modification of the matter."

It is quite generally supposed that the law of the conservation of matter was first formulated by Lavoisier, but the law was definitely enunciated by the Russian chemist Lomonossov, in 1756. Like Lavoisier, he heated tin in a closed vessel and found that there was no change in the weight of the system.

25. Experiments on the Conservation of Mass. — (1) When a candle is allowed to burn in air and the products of combustion (water and carbon dioxide) absorbed in a mixture of lime and caustic soda, as shown in Fig. 7, there is an apparent gain in weight. It has been demonstrated that this apparent increase in weight, when a candle burns, is due to the component oxygen, which is drawn in from the surrounding air. The oxygen combining with the carbon and the hydrogen of the candle was not

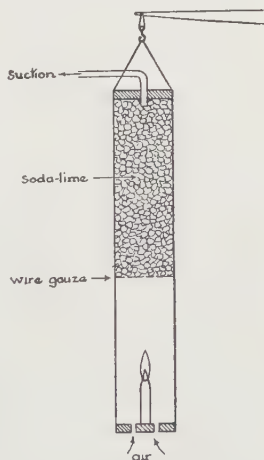


FIG. 7.

weighed in the first weighing. When this factor is taken into consideration, the sum of the weights of the factors is equal to the sum of the weights of the products.

(2) An aqueous solution of lead nitrate is poured into a flask, and a small tube containing a solution of potassium chromate is placed inside the flask so that the liquids do not mix, as shown in Fig. 8. The flask is tightly stoppered, carefully counterpoised on the balance, and is then tilted until the liquids mix. A chemical change occurs instantaneously, but the weight of the system remains constant. The lead nitrate and the potassium chromate interact to form potassium nitrate (soluble) and lead chromate, an insoluble yellow compound.



FIG. 8.

The Law of the Conservation of Mass, or the Law of the Indestructibility of Matter, may be stated as follows: The mass of a system is unaltered by any chemical change that occurs within it; or, when a chemical process is carried out, the total mass of the reactants is equal to

the total mass of the products of reaction.

Many very careful experiments have been carried out to test the validity of the law. In 1893 Landolt began a series of experiments which were not completed until 1908. After a close examination of fifteen different reactions, he failed to observe a variation in weight greater than that within the limits of experimental error.

Every chemical equation is based upon the law of the conservation of mass, so it is one of the most fundamental laws of chemistry.

26. The Law of Definite (Constant) Proportions. — We have seen (10) that a particular compound always contains the same elements chemically united in the same proportions by weight: *e.g.*, water contains 11.19 per cent of hydrogen and 88.81 per cent of oxygen. These percentages hold definitely wherever pure water is synthesized or decomposed.

The law may be illustrated experimentally by determining the percentage composition of copper oxide. This may be done by heating a known weight of copper in the presence of oxygen until the metal is transformed completely into copper oxide. Since the weight of copper oxide is equal to the sum of the weights of the copper and oxygen which unite, the weight of oxygen uniting with the copper may be found by subtracting the weight of the copper from the weight of the copper oxide.

The condensed statement is as follows:

- (1) Copper + Oxygen = Copper oxide,
- (2) Copper oxide - Copper = Oxygen.

Knowing the weights of the copper and oxygen which unite, it is very simple to calculate the percentage of each element in copper oxide.

LECTURE-ROOM EXPERIMENT

A small quantity of finely divided copper was introduced into a weighed porcelain boat, the boat and its contents carefully weighed, and then the boat was placed in a hard-glass tube (see Fig. 9), gradually raised to a high temperature, while a stream of oxygen was passed through the tube until the boat and its contents no longer gained in weight. The calculation was made as follows:

Boat + Copper = 4.256 grams	
Boat = 3.010 "	
<hr/>	
Wt. of Copper = 1.246 grams	
Boat + Copper oxide = 4.566 grams	
Boat = 3.010 "	
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Wt. of Copper oxide = 1.556 grams	
Copper = 1.246 "	
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Wt. of Oxygen = 0.310 gram	

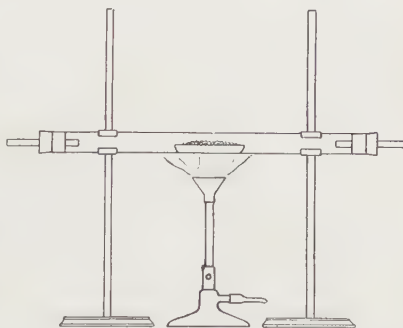


FIG. 9.

- (1) Wt. of Copper oxide : Wt. of Copper = 100 per cent : x per cent;
therefore, $x = 80.08$, which is the per cent of copper.
- (2) Wt. of Copper oxide : Wt. of Oxygen = 100 per cent : y per cent;
therefore, $y = 19.92$, the per cent of oxygen.

The most accurate experiments show that pure copper oxide always contains 79.9 per cent of copper and 20.1 per cent of oxygen. In other words, it has a constant composition by weight. This is also true of all other chemical compounds.

As the result of thousands of experiments, chemists have reached the conclusion that a particular compound always contains the same elements chemically united in the same proportions by weight. This is known as the Law of Definite or Constant Proportions, or the Law of Constant Composition.

27. **Historical.** — Wenzel (1740–1793) showed that a base and an acid combine in definite proportions by weight to form a salt.

The doctrine of combining proportions by weight was mainly established by the researches of J. B. Richter (1762–1807).

At the beginning of the nineteenth century, C. L. Berthollet and J. L. Proust carried on a celebrated controversy concerning the composition of compounds. Berthollet held that, in general, the composition of the product would vary with that of the original mixture. Proust held that the composition of a chemical compound is perfectly definite, and he conducted very careful experiments from 1799–1807. Proust was right, and is therefore regarded to be the discoverer of the law of constant or definite proportions.

28. **The Law of Multiple Proportions.** — This law was enunciated by John Dalton (1802–4). Dalton analyzed the gases ethylene and methane and reached the conclusion that, for the same quantity of carbon by weight, twice as much hydrogen was contained in the latter compound as in the former. Dalton also investigated other pairs of substances, such as carbon monoxide and carbon dioxide.

The following illustrations show that chemical combination is an orderly process, and is restricted to certain fixed proportions of matter by weight.

(1) The relative proportions by weight of carbon and oxygen in the two oxides of carbon are as follows:

	<i>Carbon</i>	<i>Oxygen</i>
Carbon monoxide.....	12	16 = 1×16
Carbon dioxide.....	12	32 = 2×16

This means that, for the same weight of carbon, carbon dioxide contains twice as much oxygen as does carbon monoxide.

(2) As another example we may take the compounds of nitrogen and oxygen, of which five are known. The percentage composition by weight of these five compounds is found by analysis to be as follows:

	(1)	(2)	(3)	(4)	(5)
Nitrogen.....	63.65	46.68	36.86	30.45	25.94
Oxygen.....	36.35	53.32	63.14	69.55	74.06
	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00

If we calculate how much oxygen is contained in each of these compounds combined with a fixed weight of nitrogen, say, 10 parts, we find that the oxygen is represented by the numbers 5.7, 11.4, 17.1, 22.8, and 28.5. By dividing these numbers by

5.7, we see that the relative quantities of oxygen are in the ratio of the simple whole numbers 1, 2, 3, 4, and 5.

The Law of Multiple Proportions may be stated thus: When two elements, A and B, unite to form more than one compound, the masses of B which unite with a fixed mass of A, stand to each other in the ratio of whole numbers, which are usually small.

29. Combining Weights of the Elements. — We have seen that, when chemical compounds are formed or decomposed (10–11), the weight relations between the elements and their compounds are definite. In other words, when we measure the combining proportions by weight of the elements in a compound, say, copper and oxygen in copper oxide (26), we find that the weights can be expressed by definite numbers. The weights of various elements which interact with fixed weights of other elements can be expressed in percentages, or they may be referred to the weight of some other element taken as standard, *e.g.*, 8 parts by weight of oxygen. Now, the chemist has found by experiment the weights of other elements which combine with 8 parts by weight of oxygen. It is convenient to refer to the fixed scale of oxygen taken as 8, for oxygen combines directly with most of the other elements. Moreover, when oxygen is taken as 8, the weight of any other element combining with 8 parts of oxygen is never less than 1.

First of all, the chemist determines by analysis or synthesis the percentage composition of compounds containing the elements.

The following numbers represent the results obtained by the analysis or synthesis of several common compounds:

Compound	Per cent	Per cent
Copper oxide.....	Copper.....79.9	Oxygen.....20.1
Water.....	Hydrogen.....11.19	Oxygen.....88.81
Aluminium oxide.....	Aluminium.....52.94	Oxygen.....47.06
Sodium oxide.....	Sodium.....74.19	Oxygen.....25.81
Chlorine monoxide.....	Chlorine.....81.59	Oxygen.....18.41
Carbon dioxide.....	Carbon.....27.27	Oxygen.....72.73

The sum of the constituents is 100 per cent. The weight of each element combining with 8 parts of oxygen can be readily calculated thus:

Per cent of Oxygen : Per cent of other Element = 8 : x .
In the case of copper oxide we have: 20.1 : 79.9 = 8 : x , whence

$x = \frac{79.9}{20.1} \times 8 = 31.8$. We therefore find that 31.8 parts by

weight of copper combine with 8 parts by weight of oxygen to form copper oxide. When the weights of the other elements are calculated in a similar way, it is found that they are as follows: hydrogen, 1.008; aluminium, 9; sodium, 23; chlorine, 35.46; carbon, 3. These combining weights of the elements referred to the scale of oxygen = 8 are known as equivalent weights, for they are chemically equivalent to each other; that is to say, the weights of the various elements found combine with, or are chemically equivalent to, 8 parts by weight of oxygen. Summing up our results we have:

Equivalent Weights

Oxygen.....	8
Copper.....	31.80
Hydrogen.....	1.008
Aluminium.....	9.00
Sodium.....	23.00
Chlorine.....	35.46
Carbon.....	3.00

The equivalent weight of an element is the weight of the element which combines with 8 parts by weight (grams) of oxygen. The term equivalent weight is definite and fixed, for it always refers to oxygen taken as 8.

The expression "combining weights" is a general one, however, for it can be employed to express the proportions by weight by assigning values to oxygen other than 8. Thus, oxygen might have the value 16, or any other multiple of 8, assigned to it. Indeed, we could arbitrarily assign to oxygen any number.

By an examination of the equivalent weights of the elements given above, it is clear that the weights of the elements which combine with 8 parts by weight of oxygen are the weights which combine with each other: *e.g.*, 23 parts of sodium unite with 35.46 parts of chlorine to form 58.46 parts by weight of sodium chloride.

30. Atomic Weights. — While chemists frequently use the equivalent weights of the elements, they much more frequently use a set of relative weights, known as the atomic weights. The reasons for so doing will be given soon. The atomic weights of the elements are identical with, or are simple multiples of, the equivalent weights, as the following table shows:

Element	Equivalent Weight	Atomic Weight
Oxygen.....	8	16
Copper.....	31.80	63.60
Hydrogen.....	1.008	1.008
Aluminium.....	9.00	27.00
Sodium.....	23.00	23.00
Chlorine.....	35.46	35.46
Carbon.....	3.00	12.00

31. The Law of Combining Weights. — When the chemist examines the composition of compounds he finds that combination always takes place between certain definite or constant proportions, or between multiples of these. This statement may be illustrated by the following table:

PROPORTIONS BY WEIGHT OF THE ELEMENTS IN CERTAIN COMPOUNDS

Compound	Copper	Oxygen	Hydrogen	Aluminium	Sodium	Carbon	Chlorine
Copper oxide.....	63.6	16
Water.....	16	2.016
Aluminium oxide.....	48	54
Sodium oxide.....	16	46
Carbon dioxide.....	32	12
Chlorine monoxide...	16	70.92
Sodium chloride.....	23	35.46
Aluminium chloride..	27	106.38
Sodium hydroxide....	16	1.008	23
Atomic Weights.....	63.6	16	1.008	27	23	12	35.46

An examination of the table shows that the weights of the elements representing the composition of compounds are either their atomic weights or these weights multiplied by whole numbers. These compounds are typical of the other compounds. The proportion, then, of each element in a compound can be represented by a fixed number, multiplied when necessary by the proper whole number.

The Law of Combining Weights may now be stated as follows: To each element may be assigned a fixed number found by experiment, which in itself, or when multiplied by some whole number, represents the weight of the element that enters into combination with other elements to form compounds.

32. Historical. — The Law of Combining Weights, which was formerly known as the Law of Reciprocal Proportions, was first formulated by the German chemist, J. B. Richter, who was busy with his researches from 1792—

1799. Richter was the originator of Stoichiometry, or "The Art of Measuring Chemical Elements."

Dalton endeavored to determine the atomic weights, or rather the combining weights, of the elements.

Berzelius, Stas, and others extended the work of Richter. According to Sir H. E. Roscoe, Cavendish (1731-1810) introduced the term "equivalent" into science. Wollaston (1766-1828) published his opinion, in 1808, that the numbers found by Dalton were not the atomic weights but the chemical equivalents of the elements.

EXERCISES

1. Define specific physical property. Mention a number of specific physical properties of sulfur, gold, iron, water, and sugar.

2. How would you distinguish between silver and platinum? gold and brass? wheat flour and starch? common salt and calomel? quartz (rock crystal) and diamond?

3. How would you distinguish between a pure substance and a mixture?

4. How does an ordinary solution, such as sugar in water, differ from a mechanical mixture, such as old-fashioned gunpowder? How may gunpowder be separated into its components?

5. When two or more substances are brought in contact, how would you know whether they interacted chemically, or simply remained mechanically mixed?

6. Mention some chemical changes which occur in nature other than those mentioned in the book.

7. When a copper wire is dipped into a solution of a salt of mercury, it soon takes on a silvery luster. Explain.

8. Cite cases of synthesis (combination) and of decomposition which we have not thus far discussed.

9. What is your conception of a chemical element? In what two senses is the term element employed? What is a compound?

10. A bar of gold 10 cm. long, 2 cm. wide, and 1 cm. thick weighs 386 g. What is the density of gold?

11. Marble has a density of 2.71 and a piece of it weighs 73.25 g. What is its volume?

12. If you were offered a "gold brick" which on the surface appeared to be gold, how could you settle the question of its purity without removing its surface or resorting to chemical tests?

13. Can you think of any objection to the statement that "the sum total of matter in the universe is constant"?

14. State two laws of chemical combination and cite experimental evidence in their support.

15. Carbon and oxygen unite to form two compounds having the following percentage composition:

	(1)	(2)
Carbon	42.86	27.27
Oxygen	57.14	72.73
	<hr/> 100.00	<hr/> 100.00

Show that we have here to do with the law of multiple proportions. [The atomic weight of carbon is 12 and of oxygen 16.]

16. Outline the "candle experiment" and point out what it teaches.

17. Making use of the information given in the table in section 31, show the number of atoms in a molecule of each of the following compounds: sodium oxide, chlorine monoxide, aluminium chloride, aluminium oxide, and sodium hydroxide.

18. 2.61 g. of aluminium were burned in oxygen and the product (aluminium oxide) weighed 4.921 g. What is the percentage composition of the compound and the equivalent weight of the metal? [Atomic weight of aluminium is 27 and of oxygen 16.]

19. Define the following terms: mass, weight, gram, kilogram, density, combining weight, equivalent weight.

READINGS AND REFERENCES

MELLOR. Modern Inorganic Chemistry, Chaps. I and II.

MOORE. A History of Chemistry, Chap. VII.

OSTWALD. The Principles of Inorganic Chemistry, Chaps. I and II.

CHAPTER II

THE ATOMIC THEORY. SYMBOLS, FORMULAE, AND EQUATIONS

33. **The Atomic Theory.** — The structure of matter engaged the attention of philosophers of the East long before the days of Grecian philosophy. Kanada, the founder of a system of Hindu philosophy, taught that matter was made up of exceedingly small, indivisible, eternal particles called **atoms** (Greek, meaning *uncut, indivisible*), which were supposed to be in perpetual motion and separated from one another by void space.

The ancient Greek philosophers were divided into two schools. On the one hand there was the school of Aristotle (384–322 B.C.), called the Peripatetic, because the pupils received instruction while walking in the Lyceum at Athens, who taught that matter is infinitely divisible. On the other hand, the school of Atomistic philosophers, led by Democritus, held that matter is finitely divisible — *i.e.*, composed of atoms. Democritus (470–360 B.C.) taught that atoms of different sizes and forms, floating about in the void, impinge on one another, the atoms of similar form tending to group themselves together. The theory of the Atomistic philosophers contained the germ of the modern theory of the structure of matter.

Sir Isaac Newton (1642–1727) had the idea that matter was formed in solid, hard, impenetrable, movable particles; and that these primitive particles are incomparably harder than any porous bodies compounded of them.

The speculation of ancient philosophers was virtually all that was known about the structure of matter until the beginning of the nineteenth century, when John Dalton (1766–1844), a school-master of Manchester, England, quickened the dead dogma of the early speculators into a living hypothesis. The essence of Dalton's atomic theory, which was formulated at the very beginning of the nineteenth century (about 1803), may be stated as follows:

(1) *Every element is made up of exceedingly small, indivisible particles called atoms.*



JOHN DALTON (1766-1844).



JÖNS JAKOB BERZELIUS (1779-1848).

(2) *The atoms of different elements possess different weights, but those of a particular element are homogeneous and constant in weight.*

(3) *Chemical compounds are formed by the union of the atoms of different elements in the simplest numerical proportions.*

34. The Atomic Theory Explains the Laws of Chemical Combination. — This theory explains satisfactorily the law of definite proportions. Let us suppose, to illustrate, that the smallest particle of carbon monoxide imaginable consists of one atom of carbon and one of oxygen in chemical union. If we assume that carbon atoms are indivisible, homogeneous, and of constant mass or weight, and that atoms of oxygen are the same, except that the mass of this atom is different from that of the carbon atom, it is clear that carbon monoxide would have a constant composition; for any particular mass of the compound, say, 1 g., would be made up of a very large number of particles of carbon monoxide, each of which contains one atom of carbon and one of oxygen.

The particles formed by the union of atoms are called **molecules** (Latin, a *little mass*). Thus, a molecule of carbon monoxide is assumed to contain one atom of carbon and one of oxygen. When we examine the composition of water, we find that the smallest particle (molecule) of the compound contains two atoms of hydrogen and one of oxygen. Likewise, the smallest particles of other compounds contain a whole number of atoms; hence compounds have a definite or constant composition.

The reader has seen (28) that, for the same quantity of carbon, carbon dioxide contains twice as much oxygen as carbon monoxide. If we assume that a molecule of each compound contains one atom of carbon, and that a molecule of carbon monoxide contains one atom of oxygen while that of carbon dioxide contains two, their compositions may be represented thus:

AB , carbon monoxide,
 AB_2 , carbon dioxide.

This is a satisfactory explanation of the law of multiple proportions.

An examination of the table showing "Proportions by Weight of the Elements in Certain Compounds" (31) makes it clear that the composition of a compound may be represented by means of a definite number of atomic weights. Thus, the composition of aluminium oxide is represented by taking two atomic weights ($2 \times 27 = 54$) of aluminium and three of oxygen ($3 \times 16 = 48$).

In general, the proportion of each element in a compound can be represented by a fixed number (atomic weight), multiplied when necessary by the proper whole number. This is the law of combining weights (31).

Each element has a fundamental number assigned to it which is called an atomic weight. Since atomic weights are only relative, and not the absolute weights of the atoms, we can express them in terms of any unit we please. The usual standard of reference is oxygen = 16.

Dalton's original atomic theory has been somewhat modified. The term molecule was not used by Dalton, but was introduced by the Italian physicist, Avogadro, in 1811.

The atomic theory appears to rest upon a firm foundation despite the fact that it has been necessary to modify it somewhat on account of the discovery of new facts, such as have to do with radium and other radioactive elements (Chap. IV). There is much independent proof that atoms and molecules really exist, and chemists even know something about the structure of atoms.

35. Hypothesis, Theory, and Law. — In order to explain certain facts and phenomena, the imagination is brought into play and hypotheses are advanced. An **hypothesis** is a conjecture at the truth — a supposition. Thus, Dalton laid down the hypothesis that all matter is made up of indivisible particles called atoms. Hypotheses prompt experiments, but they frequently prove to be erroneous and are discarded.

When an hypothesis is extended in scope and assumes a high degree of probability, it becomes a **theory**: *e.g.*, the atomic theory, the kinetic theory. A theory is a proposed explanation designed to account for things which occur. While theories deal with the fundamental principles underlying a science and attempt to account for them, they frequently involve speculation, and may be partially or wholly discarded when more facts are discovered.

A **law** is a condensed statement, or generalization, which sums up all that is found to be true in the cases examined: *e.g.*, the law of the conservation of mass. A law is a rule of the universe, or a fundamental rule of operation, or the uniform occurrence of natural phenomena in the same way, or under the same conditions. In order that a law may be true, it must be in harmony with the facts.

36. The Inductive Method in Science. — The accepted definition of **induction** (Latin *inducere*, to lead into) is that it is "the process of discovering a general principle by the observation of

particular instances." Phenomena serve as indications to aid the investigator in framing the hypothesis, generally a guess at first. The provisional hypothesis is then verified by experiment and by the collection of additional facts. The investigator has not time to examine all cases arising under any particular generalization, for too much labor would be involved. A limited number of well-chosen and carefully conducted experiments may serve to establish an hypothesis, a theory, or a law; but it must be borne in mind that they are all on probation. Induction, then, is "the ascent from particulars to generals." Ostwald says that the whole of natural science is built up of inductive conclusions.


The process of reasoning called **deduction** (Latin *deducere*, to lead or take away) starts with a general principle and derives from it facts which are necessarily involved in it; it is "the descent from general principles to particulars."

37. Names and Symbols of the Elements. — A great many of the elements have been given names derived from the Greek: *e.g.*, *hydrogen* (*water-producer*); *chlorine* (*yellowish-green*); *iodine* (*like a violet* — from its violet vapor); *helium* (*the sun* — from its occurrence in the sun). Some elements are named after particular localities: *e.g.*, *strontium*, from Strontian in Scotland. *Platinum* owes its name to the Spanish "plata," silver; *tellurium*, from Latin *tellus*, the earth; etc.

Metals end, as a rule, in *-um* or *-ium*. Thus, *aurum* (gold), *ferrum* (iron), *sodium*.

The names of non-metals generally end in *-gen*, *-ine*, or *-on*: *e.g.*, oxygen, chlorine, carbon.

The constant use of the full names of the elements would be rather burdensome; therefore it is the universal custom of chemists to use an abbreviation or a symbol.

The alchemists used crude symbols to represent different substances. Thus, gold was represented by the symbol \odot or , for the sun; silver, by D , the moon. The symbol ∇ was used by Lavoisier for water. Dalton represented the atoms of elements by symbols, which he combined to represent the elements in a particular compound: *e.g.*, \odot stood for hydrogen; \bigcirc for oxygen; etc. Water was represented by $\odot\bigcirc$. These symbols were too cumbrous, so they have all been abandoned.

In 1811, J. J. Berzelius, the great Swedish chemist, introduced a set of symbols for the elements, which are used at the present time. The universal practice is to use one or two letters of the name of the element — often from the Latin or the Greek name.

Thus, Au indicates the element gold, or *aurum*, while Fe represents iron, *ferrum*. Such abbreviations are called symbols. Au and Fe are the symbols for gold and iron, respectively.

NAMES OF THE MOST COMMON ELEMENTS, TOGETHER WITH THEIR SYMBOLS AND ATOMIC WEIGHTS

Elements	Sym- bol	Atomic Weight	Elements	Sym- bol	Atomic Weight
Aluminium.....	Al	26.97	Magnesium.....	Mg	24.32
Antimony (<i>Stibium</i>)....	Sb	121.77	Manganese.....	Mn	54.93
Argon.....	A	39.94	Mercury (<i>Hydrargyrum</i>)..	Hg	200.61
Arsenic.....	As	74.96	Molybdenum.....	Mo	96.0
Barium.....	Ba	137.37	Nickel.....	Ni	58.69
Beryllium.....	Be	9.02	Nitrogen.....	N	14.008
Bismuth.....	Bi	209.0	Oxygen.....	O	16.00
Boron.....	B	10.82	Palladium.....	Pd	106.7
Bromine.....	Br	79.92	Phosphorus.....	P	31.03
Cadmium.....	Cd	112.41	Platinum.....	Pt	195.23
Calcium.....	Ca	40.07	Potassium (<i>Kalium</i>)....	K	39.1
Carbon.....	C	12.000	Radium.....	Ra	225.95
Chlorine.....	Cl	35.46	Selenium.....	Se	79.2
Chromium.....	Cr	52.01	Silicon.....	Si	28.06
Cobalt.....	Co	58.94	Silver (<i>Argentum</i>).....	Ag	107.88
Copper (<i>Cuprum</i>).....	Cu	63.57	Sodium (<i>Natrium</i>).....	Na	23.
Fluorine.....	F	19.00	Strontium.....	Sr	87.63
Gold (<i>Aurum</i>).....	Au	197.2	Sulfur.....	S	32.06
Helium.....	He	4.002	Tin (<i>Stannum</i>).....	Sn	118.70
Hydrogen.....	H	1.008	Titanium.....	Ti	47.90
Iodine.....	I	126.93	Tungsten (<i>Wolfram</i>)....	W	184.0
Iron (<i>Ferrum</i>).....	Fe	55.84	Uranium.....	U	238.17
Lead (<i>Plumbum</i>).....	Pb	207.22	Zinc.....	Zn	65.38

A full list of the elements, with their symbols and atomic weights, is to be found inside the cover of this book.

The student should note the exact meaning of the symbols. O stands for 16 parts by weight, or one atom, of oxygen. H stands for 1.008 parts by weight, or one atom, of hydrogen. Fe stands for 55.84 parts by weight, or one atom, of iron. 3O stands for three atoms of oxygen, or 48 parts by weight.

As the symbols stand for parts by weight of the different elements, we can express the weights in grams, if we like, obtaining the atomic weight in grams, or the **gram-atomic weight**. Thus, the gram-atomic weight of oxygen is 16 g.

38. **Formulae.** — We have seen that elements combine to form compounds (19); also, that the particles formed by the union of atoms are called **molecules** (34). *Molecules, then, may be regarded as clusters or aggregates of which the atoms are the units.*

Chemists represent a molecule of a substance by a combination of symbols, which is known as a **chemical formula**. Thus, iron and sulfur (10) combine to form the product ferrous sulfide:



FeS stands for a molecule of ferrous sulfide, consisting of one atom of iron and one of sulfur.

The formula H_2O represents a molecule of water, *i.e.*, a compound containing two atoms of hydrogen and one of oxygen per molecule; CO stands for one molecule of carbon monoxide, and CO_2 for one of carbon dioxide.

Chemists have the best of reasons for believing that free oxygen gas consists of molecules composed of two atoms in chemical union: $\text{O} = \text{O}$, or O_2 . That the molecule of oxygen is diatomic will be shown in a subsequent chapter. The hydrogen, chlorine, and nitrogen molecules are also diatomic: H_2 , Cl_2 , N_2 .

$3\text{H}_2\text{O}$ stands for three molecules of water, etc. A formula has both a qualitative and quantitative significance.

The sum of the weights of the atoms in a molecule gives what is known as a **molecular weight**. Thus, the molecular weight of water is equal to $(2 \times 1.008) + 16 = 18.016$. This means that 18.016 parts by weight of water contain 2.016 parts of hydrogen and 16 parts of oxygen: *e.g.*, 18.016 g. of water when decomposed yield 2.016 g. of hydrogen and 16 g. of oxygen.

The molecular weight of a substance, expressed in grams, is known as a **gram-molecular weight**, or **mol**: *e.g.*, the molecular weight of carbon dioxide (CO_2) is $12 + (2 \times 16) = 44$; hence 44 g. of carbon dioxide is a gram-molecular weight.

39. Derivation of Chemical Formulae from Experimental Data.—We saw in the lecture-room experiment (26) that 1.246 g. of copper united with 0.310 g. of oxygen to form 1.556 g. of copper oxide. How may the simplest formula representing the composition of copper oxide be found? [The atomic weight of copper is 63.57 and that of oxygen, 16.]

Weights of the Elements	Gram-Atomic Weights of the Elements	Ratio of Atoms in the Molecule
Copper.....1.246 g.	63.57 g.	$1.246 \div 63.57 = 0.0196$
Oxygen.....0.310 g.	16.00 g.	$0.310 \div 16.00 = 0.0194$

The quotients are related to each other (very nearly) as 1 : 1, showing that for every atom (or gram-atomic weight) of copper

there is one of oxygen; hence the simplest formula of copper oxide is CuO .

In deriving chemical formulae, it makes no difference in what units the weights are expressed. If the percentage composition by weight of the compound is given, the derivation of the formula may be readily accomplished, as the following example will show:

A compound was analyzed and found to contain 43.39 per cent of sodium, 11.32 per cent of carbon, and 45.29 per cent of oxygen. Derive its simplest formula.

In 100 g. of the compound there are 43.39 g. of sodium, 11.32 g. of carbon, and 45.29 g. of oxygen.

Weights of the Elements	Gram-Atomic Weights of the Elements	Ratio of Atoms in the Molecule
Sodium..... 43.39 g.	23 g.	$43.39 \div 23 = 1.88$
Carbon..... 11.32 g.	12 g.	$11.32 \div 12 = 0.94$
Oxygen..... 45.29 g.	16 g.	$45.29 \div 16 = 2.82$
100.00 g.		

$1.88 : 0.94 : 2.82 = 2 : 1 : 3$; hence the formula is Na_2CO_3 (sodium carbonate).

Derive the simplest formula of aluminium oxide, which contains 52.94 per cent of aluminium and 47.06 per cent of oxygen.

Weights of the Elements	Gram-Atomic Weights of the Elements	Ratio of Atoms in the Molecule
Aluminium.... 52.94 g.	27 g.	$52.94 \div 27 = 1.96$
Oxygen..... 47.06 g.	16 g.	$47.06 \div 16 = 2.94$
100.00 g.		

$1.96 : 2.94 = 1 : 1\frac{1}{2}$. Since fractions of atoms do not take part in chemical changes, we multiply the numbers 1 and $1\frac{1}{2}$ by 2, without changing the value of the ratio, and obtain $2 : 3$. The formula is, therefore, Al_2O_3 , the simplest formula of aluminium oxide.

Example. — 2.238 g. of pure iron combined with oxygen to form 3.198 g. of dried rust (ferric oxide). Find the simplest formula of the compound.

40. Nomenclature of Compounds. — There are general rules to be followed in the naming of compounds.

When there are only two elements in a compound, the name of the second element is modified so as to end in *-ide*. Thus, CuO, copper oxide; NaCl, sodium chloride; ZnS, zinc sulfide; MgBr₂, magnesium bromide; SiC, silicon carbide; CaH₂, calcium hydride.

The names of compounds are so chosen that they shall, so far as possible, indicate their composition. Thus, to distinguish one oxide from another or others, prefixes are used:

CO, carbon monoxide; CO₂, carbon dioxide.

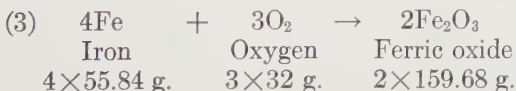
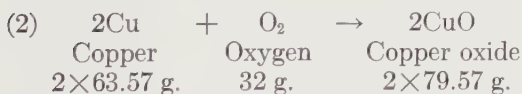
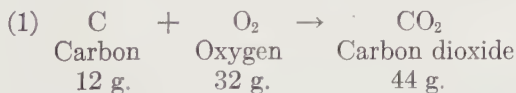
BaO, barium monoxide; BaO₂, barium dioxide (peroxide).

P₂O₃, phosphorus trioxide; P₂O₅, phosphorus pentoxide.

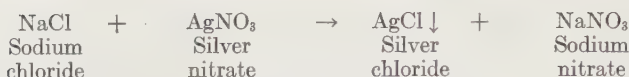
PCl₃, phosphorus trichloride; PCl₅, phosphorus pentachloride.

When an element forms with another element two well-defined series of compounds, they may be distinguished by the endings *-ous* and *-ic*. Thus, FeCl₂ is ferrous chloride and FeCl₃ is ferric chloride; FeO is ferrous oxide and Fe₂O₃ is ferric oxide.

41. **Equations.** — It has been shown that various substances interact to form other substances, and that the sum of the weights of the factors is equal to the sum of the weights of the products (25). In order to save time and to condense statements as much as possible, chemists represent chemical changes in matter by means of equations. While these equations must balance, the products and factors are different substances. The following illustrations will make this clear:



It should be borne in mind that all chemical equations are based upon the law of the conservation of mass; on each side of the equation the same elements and the same number of atomic weights must be placed, but the way in which the elements are combined with one another may be different. This is shown, for example, by the interaction of aqueous solutions of sodium chloride and silver nitrate:



Weights:

$$\begin{array}{ccccccc}
 (23+35.5) & + & (107.88+14+16 \times 3) & = & (107.88+35.5) & + & (23+14+16 \times 3); \\
 \text{or,} & 58.5 & + & 169.88 & = & 143.38 & + & 85
 \end{array}$$

The sum of the weights on either side of the equation is 228.38. This equation shows that 58.5 parts by weight of pure sodium chloride interact with 169.88 parts of silver nitrate to form definite weights of each of the products. These weights may be expressed, of course, in any unit we desire, such as grams, pounds, or tons.

EXERCISES

1. Define, and also illustrate, the following terms: atom, atomic weight, gram-atomic weight, molecule, gram-molecular weight, hypothesis, theory, law.

2. State Dalton's atomic theory and show how it explains the laws of chemical combination. How has the theory been modified?

3. Mention some of the facts which led to the discovery of the law of multiple proportions.

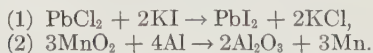
4. Who introduced the term "molecule"? Who introduced modern chemical symbols? when?

5. Explain the meaning of the following statement: "The whole of natural science is built up of inductive conclusions."

6. What symbols stand for the following elements: tungsten, antimony, argon, palladium, fluorine, uranium, manganese, strontium, molybdenum, and tin?

7. For what do the following symbols or formulae stand: Au, 3O, 3O₂, Hg₂O, HgO, As₂S₃, As₂S₆, FeO, Fe₃O₄, and Fe₂O₃?

8. Express in words the changes shown in the following equations, and write down the weights of the various substances concerned (consult a table of Atomic Weights):



9. 39 g. of an oxide of mercury were heated, and yielded 1.5 g. of oxygen. Find the formula of this oxide and the equivalent weight of mercury.

10. 2.5 g. of phosphorus burned in pure oxygen to a final weight of 5.7 g. of an oxide. Derive the simplest formula of the oxide, and then write the equation showing the chemical change when phosphorus burns.

11. 2.12 g. of copper were heated in oxygen until no further change occurred, and the resulting oxide weighed 2.652 g. Find the formula of the oxide, calculate its percentage composition, and finally the equivalent weight of copper.

12. A compound was analyzed and found to contain the following percentages: carbon, 58.5; hydrogen, 4.1; oxygen, 26.0; nitrogen, 11.4. Find its simplest formula.

READINGS AND REFERENCES

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CHAPTER III

THE LAWS OF GASES. THE KINETIC THEORY

42. **Measurement of Quantity of a Gas.** — The determination of the mass of a given quantity of a gas from its volume is complicated, because the volume changes so markedly with the pressure and the temperature. The change of volume of solids and liquids, due to a change of pressure, is so small that it is generally neglected; but in the case of gases the temperature and pressure coefficients are very large and must always be taken into account. Not only the volume but the temperature and the pressure must be measured, and from these and the density, the weight may be accurately obtained.

Gaseous volumes may only be compared when at the same temperature and pressure. Also, the density of a gas varies with the pressure and with the temperature, and it has been found necessary to select arbitrarily a *standard temperature* and a *standard pressure*.

43. **Measurement of the Pressure of a Gas.** — The pressure of a gas is most accurately and easily measured by an indirect method: a gas is brought exactly to the same pressure as the surrounding atmosphere and then the atmospheric pressure is measured with a **barometer** (Greek, meaning *weight-measurer*).

A simple barometer may be constructed as follows: A glass tube about a meter in length and 8-10 mm. in internal diameter is sealed at one end, filled with mercury and the aperture covered with the thumb; the tube is then inverted, the open end placed in a vessel containing mercury, and the thumb removed. The column of mercury sinks and finally comes to rest at a height determined by the pressure of the atmosphere, the standard being 760 mm. of mercury at 0° C. (Fig. 10).

This experiment was first performed by Torricelli, a pupil of Galileo, in 1643.

That the height of the column of mercury depends upon the pressure of the atmosphere may be shown by sucking air out of a bell-jar surrounding the lower part of a barometer (Fig. 11). The barometric column falls, of course, as the air pressure di-

minishes. This important fact was known to Robert Boyle in 1659, shortly after the air-pump was invented by Otto von Guericke.

Pascal carried out a number of experiments to ascertain if it were really the pressure of the atmosphere which sustained the column of mercury. He discovered that the barometric column



FIG. 10.

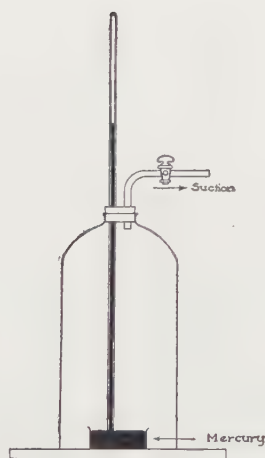


FIG. 11.



FIG. 12.

was shorter at higher altitudes; also, that the length of the column depended upon the density of the liquid used: *e.g.*, for mercury at sea level it was about 30 in., and for water, 34 ft. Mercury is 13.595 times as heavy as water, so this fact accounts for the difference.

Different kinds of barometers are in use, but one very commonly employed in the laboratory consists of a short open limb in connection with a longer one which is closed, as shown in Fig. 12. The pressure of the atmosphere is exerted on the surface of the mercury, and it sustains a column of mercury in the longer tube, which is closed. The vertical heights of the column of mercury from the surface in the longer limb to the surface in the shorter one is the pressure of the atmosphere (from *A* to *B* in Fig. 12).

The length of the column of mercury is reduced to 0°C . by applying the appropriate correction, as we shall see later.

In order to find the volume of a gas under atmospheric pressure, the vessel containing the gas (Fig. 13) is inverted in a vessel containing a liquid — usually mercury or water — and the sur-

face of the liquid in the inner vessel is adjusted at the same level as the surface of the liquid in the other vessel. The gas now being under a pressure of one atmosphere, its volume is read. The barometric reading is reduced to 0°C . by applying a correction found in the Appendix.

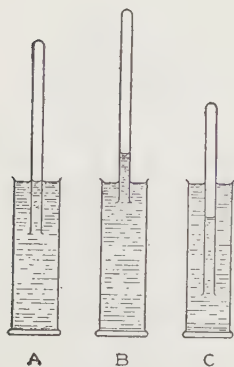


FIG. 13.

When the vessel is in position *B*, the gas is under less than atmospheric pressure; and when in position *C*, it is under more.

If, for example, the temperature of the room is 20° , the column of mercury is about 2.6 mm. longer than it would be if the barometer were standing in a room at 0° (Standard Temperature); therefore, 2.6 mm. must be subtracted from the height of the mercury column.

44. Amount of the Atmospheric Pressure. — The pressure of the atmosphere varies greatly from time to time, so it is necessary for scientists to select some pressure known as a standard (normal) pressure. **The standard pressure is 760 mm. of mercury measured at 0°C .** This is equal to 29.9217 in.

To show the variation of pressure at Princeton, it is of interest to know that on January 19, 1904, it was 782 mm. and on January 11, 1922, 726 mm. — a difference of 56 mm.

At 726 mm. water boils at 98.72° , and at 782 mm. its boiling point is 100.8° — a difference of 2.08° .

The normal pressure of the atmosphere per sq. cm. of surface is 1033.2 g. (76×13.595 . Why?) A sq. in. of surface is exposed to a pressure of approximately 15 pounds, and the pressure supported on the body of the average man amounts to about 18 tons!

45. Correction of the Volume to Standard Pressure. — Robert Boyle (1626–1691), a brilliant Irish chemist, enunciated (1660) a law governing the change in volumes of gases with change in pressure. **Boyle's Law** may be stated thus:

The temperature remaining constant, the volume of a given mass of a gas is inversely proportional to the pressure to which it is subjected. This law may be stated mathematically as follows:

$$p \propto \frac{1}{v};$$

or,
$$\frac{p_1}{p_0} = \frac{v_0}{v_1},$$

whence
$$p_1 v_1 = p_0 v_0.$$

The pressure (p) and the volume (v) of a given mass of a gas at a fixed temperature is constant:

$$pv = \text{const.}$$

This law means that if the pressure applied to a gas is doubled, the volume is halved, etc. Any change in volume due to a change in pressure may be made by a simple direct application of the law.

Example. — 25 cc. of hydrogen gas are collected under a pressure of 775 mm. Find the volume under 760 mm. of mercury.

As the volume is reduced to a lower pressure, it must become larger; hence we multiply by a fraction larger than unity:

$$v = 25 \times \frac{775}{760}.$$

46. Volumes of Gases and Temperatures. — The changes in the volume of a gas with changes in temperature are large; but before taking up the law governing these changes, the various temperature scales in use will be considered. There are three common temperature scales:

- (1) The Fahrenheit Scale, F° . (Not used in scientific work.)
- (2) The Centigrade Scale, C° .
- (3) The Absolute Scale, A° .

On the Fahrenheit scale, ice melts at 32° and water boils at 212° (under standard atmospheric pressure) — a difference of 180° . The corresponding points on the Centigrade scale are 0° and 100° — a difference of 100° . It follows, therefore, that $1^\circ F. = \frac{100}{180}$ of $1^\circ C.$, or $\frac{5}{9}$ of $1^\circ C.$

The following formulae can be used for converting one temperature to the other:

$$F^{\circ} = 9/5 (C^{\circ}) + 32, \text{ and } C^{\circ} = 5/9 (F^{\circ} - 32)$$

Problem. — Convert 21°C. to the Fahrenheit scale. Convert 90°F. to the Centigrade scale.

The **Absolute Scale** of temperature is based upon the fact that the volume of a given mass of a gas, the pressure remaining constant, will increase or decrease $1/273$ of its volume at 0°C. for every degree through which it is heated or cooled. The zero point on this scale is -273°C. , and is called the **absolute zero**. 273°A. is the same as 0°C. It follows, therefore, that $A^{\circ} = C^{\circ} + 273$. A temperature of $20^{\circ} \text{C.} = 293^{\circ} \text{A.}$ In the correction of the volume of a gas for temperature, C° must always be converted to A° .

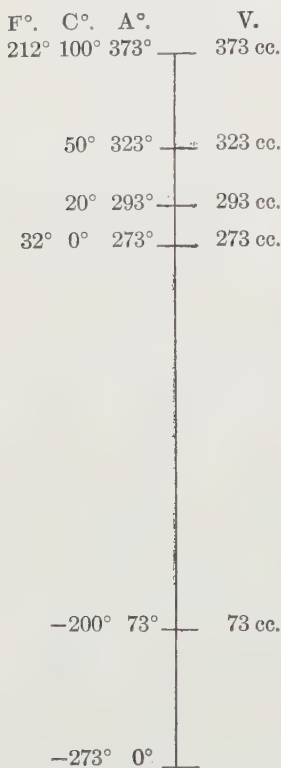


FIG. 14.

The accompanying diagram (Fig. 14) shows the relation of the temperature scales to each other, and the relation of the volumes of gases to the absolute temperature.

An examination of the diagram shows that a gas should have no volume at absolute zero, but as a matter of fact all known gases are liquid or solid before this temperature is reached. Helium is the most difficult of the gases to liquefy. Liquid helium boils at 4.5°A. , or -268.5°C. By the rapid evaporation of the liquid a temperature within 1°A. has been reached.

47. The Law of Charles. — The Law of Charles (1787) may be stated thus:

The pressure remaining constant, the volume of a given mass of a gas is directly proportional to the absolute temperature.

At constant pressure,

$$v \propto T;$$

at constant volume,

$$p \propto T.$$

The law also may be stated mathematically thus:

$$\frac{v_0}{v_1} = \frac{T_0}{T_1}.$$

In this expression v_0 is the volume of a given mass of gas at zero degrees centigrade, or T_0 absolute ($=273$); v_1 is the volume at the absolute temperature T_1 ($=273^\circ + C^\circ$).

We have seen (46) that all gases, when heated or cooled under constant pressure, expand or contract by an equal fraction of their volume at 0°C. for equal changes in temperature. The coefficient of expansion is $1/273$ for a change of 1°C.

Any change in volume of gas produced by change in temperature may be made by a direct application of the law of Charles.

Example. — 10 cc. of hydrogen are collected at 20°C. Find the volume at standard temperature ($0^\circ \text{C.} = 273^\circ \text{A.}$).

$$v_0 = 10 \times \frac{273}{(273 + 20)}.$$

We multiply by a fraction less than unity, for the gas cools down from 293°A. to 273°A.

The law of Charles was discovered independently by Dalton in 1801 and by Gay-Lussac in 1802. The experiments of Charles were not published, but were verbally communicated to Gay-Lussac.

48. Behavior of Gases under Simultaneous Action of Heat and Pressure. — Any change of volume produced by change of pressure and temperature may be made by a simple direct application of the two laws.

Example. — 25 cc. of nitrogen are collected at 21°C. and under a pressure of 750 mm. Find the volume at S.T.P.

$$v_{\text{S.T.P.}} = 25 \times \frac{273}{294} \times \frac{750}{760}.$$

Carefully inspect each fraction before making the calculation and see that it produces a change in the desired direction. If the desired temperature is lower, the volume must decrease; if the desired pressure is lower, the volume must increase.

State the conditions when the desired temperature is higher than the observed; when the desired pressure is greater than the observed.

49. **Mixed Gases: Dalton's Law.** — Dalton, in 1807, enunciated an important law which may be stated thus:

A mixture of gases, provided they do not combine chemically, exerts a pressure equal to the sum of the pressures which would be exerted by each of the components separately if allowed to fill the containing vessel alone at the particular temperature.

In other words, the pressure exerted by one gas does not interfere with the pressure exerted by another; they are independent of each other. The pressure exerted by each gas is called its **partial pressure**, and the partial pressure is proportional to the concentration of the particular gas in the mixture.

When a gas is collected in a vessel standing over a liquid tending to give off vapor, some of the vapor is always mixed with the gas. Thus, when a gas is collected over water, a certain amount of water vapor is mixed with the gas. The amount of water vapor is greater at higher temperatures. *The partial pressure of the water vapor is called aqueous tension, or the vapor pressure of water.*

The presence of moisture in a gas makes its volume larger than the volume of the dry gas, so in order to reduce the volume of a gas, measured over water, to the dry condition, *the aqueous tension is subtracted from the corrected barometric pressure.*

Example. — 25 cc. of oxygen, measured over water at 20° C. and under a pressure (corrected) of 765 mm., would occupy what volume when reduced to the dry condition and to S.T.P.?

Note. — The aqueous tension at 20° C. = 17.4 mm.

$$V_{\text{S.T.P.}} = 25 \times \frac{273}{293} \times \frac{(765 - 17.4)}{760}.$$

50. **Diffusion of Gases: Graham's Law.** — When a cylinder containing hydrogen is placed mouth downward above another cylinder containing air, the particles of hydrogen, despite their lightness, move downward and penetrate into the air, and the air moves upward and penetrates into the hydrogen. This movement of the gases goes on until a homogeneous mixture is obtained. The molecules of gases possess independent power of locomotion. The phenomenon described is known as *diffusion*. As hydrogen is the lightest gas, it diffuses most rapidly. The diffusion of hydro-

gen may be illustrated by the apparatus shown in Fig. 15. A porous clay cup is fitted with a rubber stopper from which a tube passes to a bottle containing a colored solution. A glass tube drawn out to a jet dips into the solution. If a large beaker or bell-jar containing hydrogen is lowered over the porous cup, hydrogen diffuses into the cup more rapidly than the slower moving air diffuses out, and the increase of pressure produces a fountain.

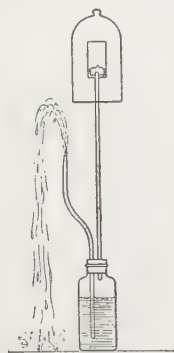


FIG. 15.

Graham (1833) enunciated a law governing the rates of diffusion of gases. The **law of Graham** may be stated thus:

The rate or speed of diffusion of a gas is inversely proportional to the square root of its density.

Thus, oxygen is approximately 16 times as dense (heavy) as hydrogen; hence their rates of diffusion are as follows:

Rate of Diffusion of Hydrogen : Rate of Diffusion of Oxygen = $\sqrt{16} : \sqrt{1}$, or as 4 : 1. This means that hydrogen diffuses four times as rapidly as oxygen.

Gases in general, when allowed to mix, behave as do hydrogen and oxygen. Diffusion of gases is very important. Thus, when a toxic or an evil-smelling gas escapes into the air, diffusion sets in and the gaseous molecules become so highly dispersed that the gas is no longer noxious. Owing to diffusion the proportions of nitrogen and oxygen in the air are practically constant at all elevations.

51. Density of Gases. — The **density** (absolute) of a gas may be found by determining the mass of a certain volume at the desired temperature, and then dividing the mass (M) by the volume:

$$D = \frac{M}{V}$$



FIG. 16.

The determination is carried out in a heavy round-bottomed flask, fitted with a stopper and stopcock, as represented in Fig. 16. The flask usually has a capacity of 250–300 cc. The air is first pumped out, the flask closed tightly, and then weighed. It is then filled with the pure dry gas at atmospheric pressure, the temperature and pressure noted, and

the flask with its contents weighed. The increase gives the weight of the gas at the particular temperature and pressure. The volume of the flask is determined by filling it with water and reweighing. The grams of water correspond to the capacity of the flask in cc. The volume of the gas is now reduced by rule (48) to S.T.P., and the weight (in grams) of the gas divided by its volume (in cc.) gives its normal density, *i.e.*, the density at S.T.P.

The **relative density**, or **specific gravity**, of a gas may be defined as the ratio between the weight of the substance and that of an equal volume of the standard gas when the latter is considered as unity. Oxygen, hydrogen, and air are used as standards.

Example. — Find the relative density (sp. gr.) of carbon dioxide referred to air [air = 1].

1 liter of carbon dioxide weighs 1.976 g., at S.T.P.

1 liter of air weighs 1.293 g., at S.T.P.

$$\text{Relative density} = \frac{1.976}{1.293} = 1.53$$

THE KINETIC THEORY

52. The Molecular Theory. — We have seen that there are three states of matter — the solid, the liquid, and the gaseous states. We also have seen that masses are composed of exceedingly small particles called molecules, each one of which possesses the same properties as does the mass as a whole; also, that molecules are composed of atoms of elements combined in definite numbers.

It is believed by scientists that the small discrete particles (molecules) of matter are in motion. The energy of motion of molecules is called Kinetic, from a Greek word meaning “move”; hence the **Kinetic-Molecular Theory**.

Matter is either continuous or discontinuous. The behavior of matter can only be explained by assuming that it has a discontinuous structure, *i.e.*, composed of discrete particles. One proof of this is that all matter is compressible. Gases are very compressible; and when liquids are evaporated, they form large volumes of vapors (gases). Thus, when a liter of water is evaporated it yields about 1,700 liters of steam, measured at 100° and 760 mm. Liquids and solids are slightly compressible, gases are absorbed by metals, liquids dissolve in solids, etc.

According to Sir Oliver Lodge, the idea of **discontinuity** is one of the main features of modern science. He says:

“Modern science is imbued with the idea of discontinuity, since it finds that all matter is composed of atoms, that electricity is composed of electrons, and that, however continuous the ultimate medium (the ether or space) may be, the energy in it seems to travel in separate discontinuous elements called quanta.”

53. The Kinetic Theory of Gases. — The kinetic theory of gases in its present form is due chiefly to the labors of Maxwell and of Clausius. The theory was first suggested, however, by Bernoulli, in 1738. Matter in the gaseous state is the most suitable with which to begin the study of the kinetic theory, for in this form substances are characterized by very simple and uniform behavior with respect to pressure and temperature. Inasmuch as all gases are uniformly affected, we are led to believe that the constitution of this form of matter is most simple.

Below are given some of the results of observation (facts) with the corresponding deductions from the kinetic theory.

Results of Observation

- (1) A gaseous body is homogeneous.
- (2) A gas is very compressible.
- (3) Gases diffuse rapidly.
- (4) A gas exerts a pressure on the sides of the containing vessel.
- (5) A gas does not settle appreciably.
- (6) Boyle's Law.

(7) Charles' Law.

(8) Graham's law of diffusion.

Results of Theory

- (1) The molecules of a gas are closely alike.
- (2) The molecules are relatively far apart.
- (3) The molecules are in rapid motion.
- (4) Pressure is caused by impact of molecules.
- (5) The molecules must be perfectly elastic and in rapid motion.
- (6) Pressure is proportional to the concentration of the gas, or the number of collisions of the molecules of a given mass of a gas with the walls of the confining vessel are inversely as the volume.
- (7) Rise in temperature increases the velocity of the molecules and therefore the kinetic energy, or the kinetic energy is directly proportional to the absolute temperature.
- (8) The speed of gaseous molecules is inversely proportional to the square root of their mass.

In the case of gases, the actual volume of the molecules is very small as compared with the space between the molecules. The molecules of a gas move in straight lines, and are continually striking the walls of the containing vessel and colliding with each other.

54. The Kinetic-Molecular Theory Explains the Gas Laws. — The temperature remaining constant, the pressure of a confined gas is dependent upon the number of molecules in a given volume. Thus, doubling the molecules doubles the pressure (see Fig. 17).

That the pressure of a gas is proportional to its concentration, or inversely proportional to its volume, is shown in Fig. 18. Thus, when the volume of a given mass of a gas is reduced to one-

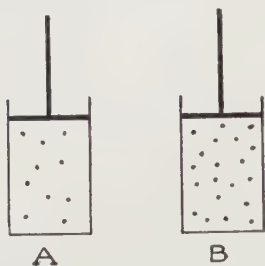


FIG. 17.

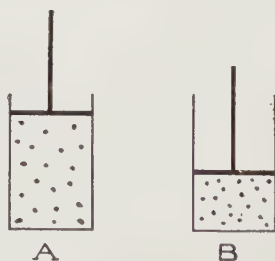


FIG. 18.

half, the pressure is doubled; for the number of impacts of the molecules is doubled in a unit of time. This is one way of stating Boyle's law.

The kinetic energy of a body of mass m moving with a speed u is $\frac{1}{2} mu^2$, and the kinetic energy of a molecule is directly proportional to its absolute temperature; or,

$$\frac{1}{2} mu^2 \propto T.$$

Therefore, when a confined gas is heated at a given pressure, the pressure can only be kept constant by allowing the gas to expand. The average molecule has to make a longer excursion before collision with the walls of the confining vessel; but the pressure may be kept constant by allowing the gas to expand, despite the increase in kinetic energy of the molecules. This is the law of Charles.

At constant temperature (T), molecules of gases possess the same kinetic energy. For gases with molecular mass of m_1 and

m_2 and with speeds of u_1 and u_2 respectively, we have:

$$\frac{1}{2} m_1 u_1^2 = \frac{1}{2} m_2 u_2^2;$$

or,

$$\frac{u_1}{u_2} = \frac{\sqrt{m_2}}{\sqrt{m_1}}.$$

Stated in words, the speed of molecules is inversely proportional to the square root of their mass (Graham's law of diffusion). It thus appears that gases exhibit a uniform behavior.

55. Avogadro's Hypothesis. — To explain the uniform behavior of gases, Avogadro (1811) made the assumption that equal volumes of different gases at the same temperature and pressure contain an equal number of molecules. The hypothesis of Avogadro has been thoroughly tested, and is now accepted as one of the most useful laws of chemistry and of physics.

56. Liquefaction of Gases. — A gas may be liquefied by cooling a mass of it to its critical temperature and by applying its critical pressure (98). Thus, oxygen liquefies at -118.8° , the pressure being 49.7 atmospheres; and carbon dioxide, at 31.35° when under a pressure of 72.85 atmospheres.

Gaseous molecules have a tendency to cohere, which is scarcely noticeable so long as a gas is warm and under ordinary pressure. When a gas is cooled, however, the speed of the molecules is lowered, and they will cohere to form a liquid if the temperature is low enough and the pressure great enough to bring the molecules sufficiently close together. Superheated steam at 374° (its C.T.) may be liquefied by applying its critical pressure.

(Why did Faraday call some of the gases "permanent" gases?)

57. Deviations from the Laws of Gases. — The laws of Boyle and of Charles are not strictly true. All known gases, except hydrogen and helium, are more compressible than they should be when subjected to moderate pressures. Under high pressures, a point is reached where all gases are less compressible than Boyle's law would lead one to expect.

The deviation from Boyle's law for several gases is shown in the following table:

Volumes filled at 0° by two liters of each gas when the pressure is raised from 1 atmosphere to 2 atmospheres:

Hydrogen.....	1.0006 liters
Oxygen.....	0.9995 "
Carbon dioxide.....	0.9931 "
Ammonia gas.....	0.9845 "
Sulfur dioxide.....	0.9739 "

The deviation from Boyle's law can be explained in terms of the kinetic theory. When gases under atmospheric pressure are subjected to moderate pressures, cohesion becomes more marked, for the molecules are brought closer together. Under very high pressures, the molecules are brought so close together that their volumes fill a considerable portion of the space; consequently the gases are less compressible than they should be according to Boyle's law. Gases, such as sulfur dioxide and ammonia, which liquefy easily deviate most from the law.

Charles' law is not strictly true. The coefficient of expansion with increase in temperature is considerably larger than one would expect for gases which may be readily liquefied. According to the law of Charles, the normal coefficient of expansion is about¹ $1/273$, or 0.003663 (47). Hydrogen, air, oxygen, nitrogen, and helium depart very little from a perfect gas. Thus, the coefficient for air is 0.003665 and for hydrogen, 0.003663. The coefficient of expansion for carbon dioxide is 0.0037, for this gas can be more easily liquefied.

All known gases, then, deviate more or less from the laws of gases. In discussing the deportment of gases, an imaginary gas, termed a **perfect gas**, is often referred to; it exhibits no deviation from the laws.

58. **Gas Statistics.** — The kinetic theory has made it possible for scientists approximately to compute magnitudes in the molecular world.

(1) Diameter of molecules. It has been computed that it would take about 40,000,000 molecules, touching one another, to make a row one inch long.

(2) Number of molecules. It has been found that there are 2.7×10^{19} molecules in 1 cc. of a gas at S.T.P., with a probable error of less than 1 per cent.

(3) Velocity per second. The following numbers are the mean velocities of a few gases at 0°:

Hydrogen.....	1,859 meters, or 1.15 mi. per second.
Nitrogen.....	492 "
Oxygen.....	465 "
Carbon dioxide.....	396 "
Chlorine.....	310 "

¹ To be more exact, the absolute zero is now fixed at -273.1° ; for the normal coefficient of a gas between 0° and 100° is 0.3661, and $100 \div 0.3661 = 273.1^{\circ}$.

As the hydrogen molecule is the lightest, its velocity is the greatest, being over a mile per second.

(4) Collisions per second. It has been computed that a hydrogen molecule collides, at S.T.P., with its fellows 9,520,000,000 times per second! At 20° C. (room temperature) the number rises to 10,060,000,000. It would take one individual, counting at the rate of 3 per second 24 hours per day, over a century to count this number.

According to Aston, if an ordinary electric light bulb were evacuated and a minute hole made in its side, just big enough to allow one million molecules to pass per second, it would be 100 million years before the bulb is filled with air at atmospheric pressure.¹

Small as molecules are, atoms and electrons are still smaller.

According to Sir Oliver Lodge, 250,000,000 atoms in a row would stretch something like an inch, while 100,000 electrons in a row would stretch something like an atom. Also, if the atom were magnified to the size of a cathedral, each component electron would be something like the size of a gnat (73).

59. The Kinetic Theory and Liquids. — Matter in the liquid state takes the shape of the containing vessel, while definite masses of gases are capable of indefinite expansion. Cohesion plays, therefore, a much greater rôle in the case of liquids. The densities of liquids are greater than those of gases, for the molecules of the former are much nearer one another. It follows from this that the diffusion of liquids proceeds slowly as compared with that of gases. Perhaps the molecules of liquids glide over each other in curved courses. The following experiment shows that liquids diffuse:

One end of a long crystal of potassium permanganate is fastened to a clock-glass by means of a little wax, and the other end is immersed in water contained in a tall glass cylinder. The permanganate gradually dissolves, the solution sinks, and diffusion begins. The process of diffusion proceeds rather slowly until a homogeneous liquid is finally obtained.

Evaporation proves that the molecules of a liquid are in motion. Not all molecules of a particular liquid, say, water, possess the same quantity of kinetic energy; but the molecules as a whole have a mean value. Those coming to the surface of a liquid with

¹ It must be supposed that the hole is gradually enlarged, for the increased pressure inside the bulb would lessen the number of molecules entering per second.

the greatest kinetic energy will break away from the surface, and if the molecules possess sufficient kinetic energy they will pass beyond the sphere of molecular attraction never to return. Since the warmest molecules possess the greatest quantity of kinetic energy, the temperature of a liquid falls as evaporation proceeds. Other molecules leaving the surface of a liquid would not move with sufficient speed to carry them beyond the range of molecular attraction; consequently they would plunge back into the liquid. Now, when a liquid evaporates, these opposite processes — evaporation and condensation — are always in operation. In open vessels, evaporation proceeds more rapidly, particularly at higher temperatures. A draft accelerates evaporation, for the molecules are swept away so that they cannot be dragged down into the liquid.

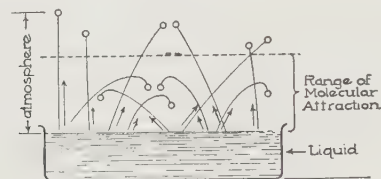


FIG. 19.

In Fig. 19 a diagrammatic representation (after Risteen) of an evaporating liquid is shown.

If a mass of liquid, *e.g.*, water, be confined at a constant temperature in a closed vessel as shown in Fig. 20, obviously a state would finally be reached when evaporation and condensation would exactly balance each other, or when the number of molecules leaving the surface of the water is equal to the number returning to the liquid state. Such a condition is known as a **kinetic equilibrium**. Both operations — evaporation and condensation — are still in full sway, but they are going on simultaneously, the one just balancing the other.



FIG. 20.

60. **The Brownian Movement.** — Robert Brown, a botanist, first observed in 1827 that when a little lycopodium (spores of the club moss) is suspended in water and examined under the microscope, the small particles appear to be in motion. Each particle moves about in a zigzag path, vibrating with a slow trembling

motion (Fig. 21). The kinetic theory furnishes the only satisfactory explanation of this phenomenon. The movement of the suspended particles appears to be due to bombardment by molecules of water. Apparently, the particles of water are in perpetual motion and are continually colliding with the particles of the suspension. The lighter the particles of the suspension, the livelier the motion. The movement is shown by all suspensions, such as carbon, gamboge, gold, and silver, provided the particles are sufficiently small. The movement of the particles may be likened to a swarm of gnats in a sunbeam.



FIG. 21.

The phenomenon of the Brownian Movement may be demonstrated according to the following instructions given by J. W. Mellor:

"Rub a fragment of gamboge for a moment on an ordinary 3×1 glass slip, and place a couple of drops of water on the slip where the gamboge has been rubbed. Gently push a cover-glass up to the edge of the gamboge. The brisk motion of the particles can now be readily seen through a $\frac{1}{2}$ " objective and a dark-ground illumination."

The experimental facts in connection with the Brownian Movement go far toward establishing the validity of the Kinetic-Molecular Theory.

That molecules of water are exceedingly small is strikingly shown by Whitney, who has calculated that if the molecules in a glass of water could each be changed into a grain of sea sand, the sand thus produced would be sufficient to cover the whole of the United States to a depth of 100 feet.

61. Molecular Relations in Solids. — A solid body retains or tends to retain the form imposed upon it by nature or by art. Like liquids, solids are characterized by much greater densities than are gases. According to the kinetic theory, a solid body is composed of particles which vibrate or rotate about centers of rest. Particles of solids tend, therefore, to keep their relative positions, while those of a liquid appear to glide over each other in curved courses, and those of a gas move in straight lines. There is no very sharp line of demarcation, however, between liquids and solids in this respect. To illustrate, there are viscous liquids, such as syrups, and so-called solids, such as cobbler's wax. All true solids tend, however, to assume crystalline forms, showing definite cleavage. That some motion takes place in solids may be shown by removing the layer of silver from an old piece of electro-

plate. The presence of this metal in the copper or German silver has been demonstrated, showing that silver had slowly diffused.

Some solids give off particles of vapor just as do volatile liquids. Thus, camphor, ice, snow, iodine, etc., evaporate spontaneously. (Why does wind assist in evaporating snow or frost?)

62. Amorphous and Crystalline Substances. — Substances may be divided into two classes — amorphous and crystalline. Under amorphous substances we have liquids and glassy solids, in which the arrangement of the particles is chaotic,¹ *i.e.*, not arranged according to a definite pattern. The arrangement of the particles may be likened to trees growing in a natural forest. A crystalline substance, on the other hand, is one in which the particles are arranged in definite order, like trees in a nursery or garden, or soldiers on parade. Crystals have a structure, and therefore many of them possess marked cleavage, as illustrated in mica. This mineral may be split into sheets of inconceivable thinness; indeed, it is estimated that a single sheet may be only two molecules in thickness! While some crystals are microscopically small, others are very large. A natural crystal was found which measured 3 feet by 6 feet by 42 feet in length, 37 tons of spodumene (lithium aluminium metasilicate) having been quarried from a single crystal. Artificial crystals do not reach these dimensions, but very long metallic crystals have been prepared. Thus, when plastic tungsten is drawn through a die at such a rate that the particles have time to arrange themselves in definite order, crystals a mile or more in length may be prepared.

A crystal may be defined as a substance bounded by plane faces at definite angles to each other and having physical properties alike along parallel directions. Crystals are formed by the solidification of a substance — elementary or compound — or by the deposition of a substance from solution. The smallest crystal which makes its appearance has the same crystalline form as a large crystal. Crystals are formed, therefore, by growth.

Crystallization may be shown most beautifully by placing a drop or two of silver nitrate solution on a clean glass slide and then adding a small piece of copper filing or of very fine copper wire. When examined, crystals of silver are to be seen — the so-called “silver tree.”

Crystalline form is very important in the identification of substances. Thus, morphine is the principal component of opium,

¹ Recent investigations appear to show a tendency in certain liquids toward molecular arrangement.

from which it may be extracted and obtained in the form of white rhombic crystals. Its crystalline form, together with its bitter taste and many color reactions, enables the chemist to identify it with certainty.

63. Classification of Crystalline Forms. — Notwithstanding the large number of crystalline forms, all crystals may be classified in six systems. These systems are readily defined by referring each to fundamental axes. They are as follows:

I. Regular (Isometric) System. Three equal and interchangeable axes at right angles. NaCl, FeS₂, PbS, etc., belong to this system; also most metals. (Fig. 22, I, and Fig. 23 A.)

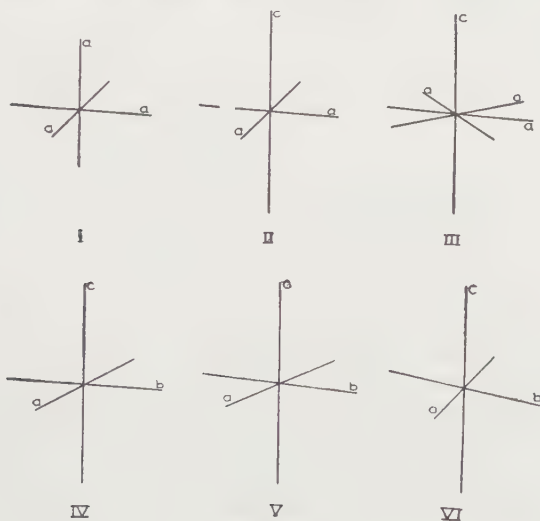


FIG. 22.

II. Square Prismatic (Tetragonal) System. Three axes, all at right angles, two of which (the lateral axes) are interchangeable and equal: *e.g.*, zircon (ZrSiO₄), nickel sulfate (NiSO₄·6H₂O). (Fig. 22, II, and Fig. 23 B.)

III. Hexagonal System. Four axes, three of which are equal and interchangeable, being in the same plane and at an angle of 60° to each other. All are at 90° to the fourth axis: *e.g.*, SiO₂ (quartz), CaCO₃ (calcite). (Fig. 22, III, and Fig. 23 C.)

IV. Rhombic (Orthorhombic) System. Three unequal axes, all at right angles: *e.g.*, KMnO₄, KNO₃, sulfur, topaz. (Fig. 22, IV, and Fig. 23 D.)

V. **Monosymmetric (Monoclinic) System.** Three axes, all unequal, two of which (the lateral) are at right angles. One of these is at right angles to the third or *C* axis; the other is inclined: *e.g.*, feldspar, rock candy, tartaric acid (Fig. 22, V, and Fig. 23 E).

VI. **Asymmetric (Triclinic) System.** Three axes, all unequal and inclined: *e.g.*, copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$). (Fig. 22, VI, and Fig. 23 F.)

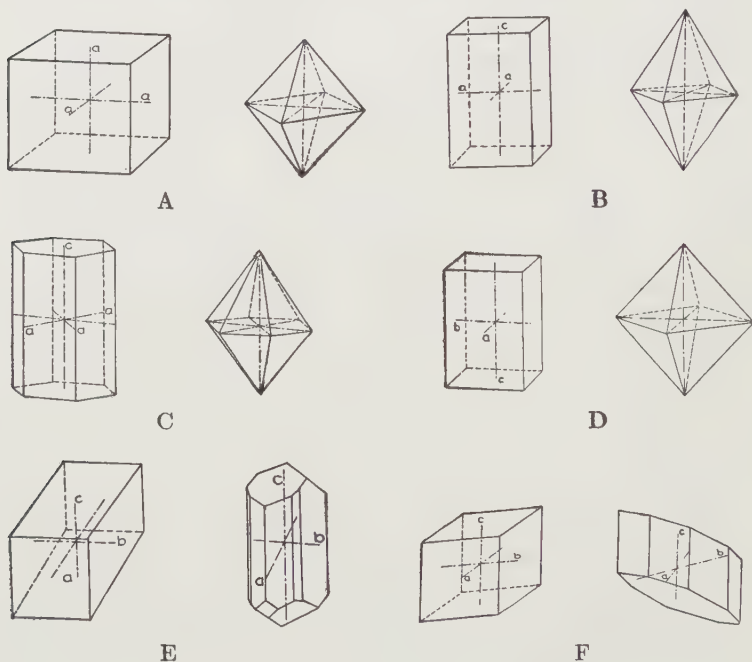


FIG. 23.

64. **The Internal Structure of Crystals.** — Visible light and X-rays are similar in nature, but the wave-lengths of the latter are very much shorter than the former. The X-rays are invisible to the eye, but affect a photographic plate. When a beam of sunlight is concentrated on a glass prism and after emerging from the prism is received on a screen, it is found to present a band of colors known as the **spectrum**. Spectra may also be produced by means of *diffraction gratings*, which are made by ruling a series of parallel and equidistant lines upon metal, glass, or the opaque film of a photographic plate. The distance apart of these lines

is of the order of the wave-length of light, there being on some gratings as many as 25,000 per inch. When such gratings are exposed to strong sunlight, diffraction spectra are produced.

When the cathode rays (streams of electrons) emanating from the cathode of a vacuum tube are suddenly stopped in their motion by striking a solid target (*e.g.*, platinum), placed at the anode, radiation from the anode occurs; that is, X-rays are produced (Fig. 24). When different elements are employed as targets, X-rays of slightly different wave-lengths are obtained and X-ray spectra are produced.

It occurred to Laue of the University of Zurich (1912) that the successive rows of particles in a crystal ought to behave toward X-rays very much as a diffraction grating does toward ordinary light. Laue's conclusion has been fully confirmed by experiment, so X-rays have been employed successfully in the study of crystal structure.

When a beam of X-rays is passed through a thin section of the crystal and then allowed to strike a photographic plate, a diffraction pattern of the crystal lattice is produced (Fig. 25).

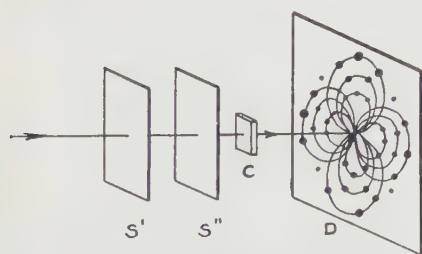


FIG. 25. Laue Method for the Determination of Crystal Structure.

A beam of X-rays is passed through pin-holes in the lead sheets S' and S'' and then broken up by the crystal C into a diffraction pattern which is registered on the photographic plate D .

Bragg and Bragg employed an X-ray spectrometer and mounted the crystal so as to use it as a reflection grating, its various faces being successively employed. From the X-ray spectra thus obtained they were able to determine the relative positions of the

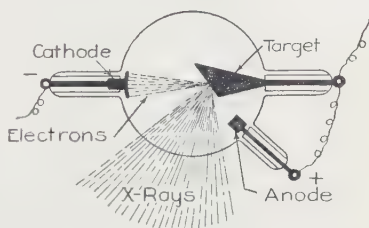
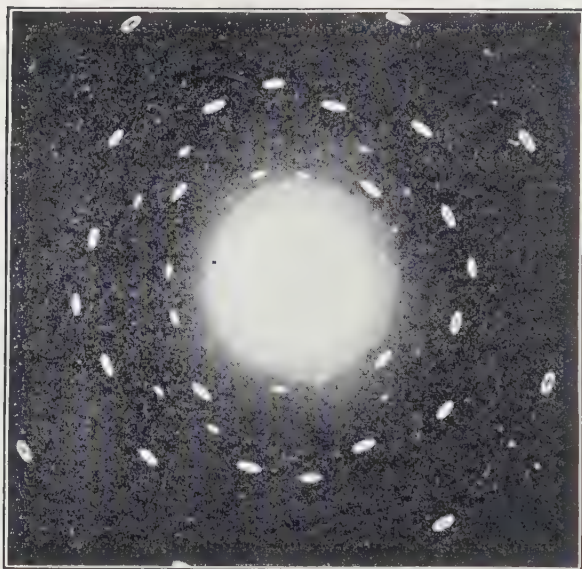
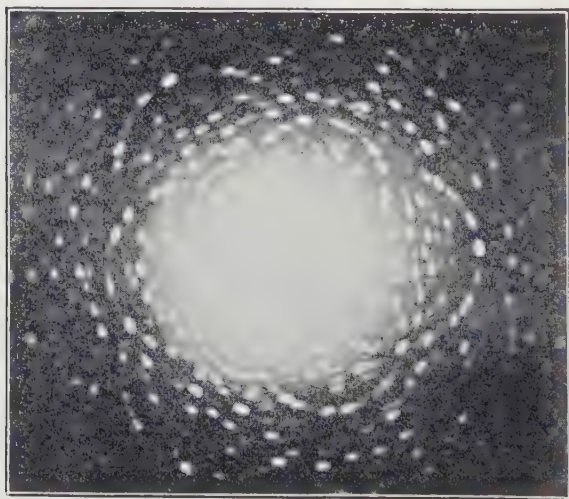


FIG. 24.

Laue, *e.g.*, made photographs of sodium nitrate, anhydrite, aragonite, potash alum (Fig. 26), etc. From the position of the crystal, its distance from the photographic plate, and its crystallographic measurements, skilled mathematicians are able to construct models of the space lattice of crystals. Each spot in a Laue photograph represents the reflection of the X-rays by a plane of the crystal lattice.



(a) Laue Diagram of Magnesium Oxide.



(b) Laue Diagram of Potash Alum.

FIG. 26.

atoms in the space lattice of the crystal. In other words, they were able to measure the distance between the rows of particles in crystals. The arrangement of atoms in a crystal of sodium chloride is shown in Fig. 27. *The structure of the crystal depends upon the arrangement of the constituent atoms and not upon that of the molecules.* The atoms, therefore, are the units that give the crystallographic pattern.

Hull, Debye, and Scherrer have independently devised a method in which the substance is employed in the form of fine powder consisting of tiny crystals. A beam of X-rays is passed through the powdered substance, the rays being diffracted to a photographic plate, where a line is produced for each kind of plane within the crystal. The crystal

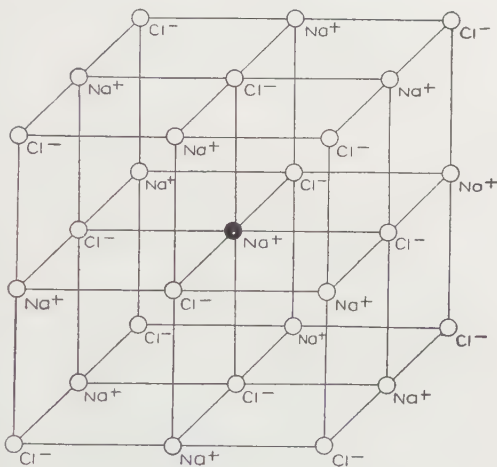


FIG. 27.

structure can be calculated from the positions and intensities of these lines.

The X-ray method has demonstrated that many elements and compounds exhibit the **cubic lattice**, which is the most symmetrical arrangement possible. There are three ways in which atoms may be arranged in three dimensions to give a lattice of this type:

(1) **The Simple Cubic Lattice** (Fig. 28). This is well illustrated by the crystal of sodium chloride. The exact arrangement of the atoms is shown in Fig. 27. Each sodium atom is surrounded by six equidistant chlorine atoms, and each chlorine atom is surrounded by six equidistant sodium atoms. It thus appears that no particular sodium atom is joined to a particular chlorine atom to form a molecule of sodium chloride. It has been demonstrated that the atoms of common salt are electrically charged. Each chlorine atom has gained an electron, or a negative particle of electricity, while each sodium atom has lost an electron, or is positively charged. No doubt the very strong attractive and

repulsive forces between unlike and like atoms have much to do with the prevention of disintegration. A compound of the type of sodium chloride is known as a *polar compound* (88).

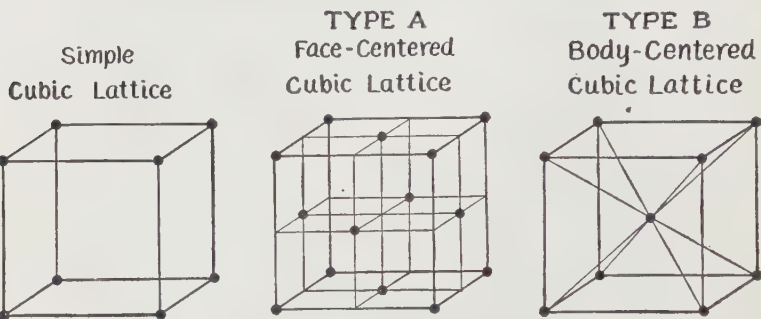


FIG. 28. Cubic Lattices.

It may be stated in general that substances which crystallize in cubes, are built up of a cubic lattice. Potassium chloride, magnesium oxide, and calcium sulfide are similar to sodium chloride.

(2) **The Face-centered Cubic Lattice** (Fig. 28). This arrangement of atoms is exhibited by copper, silver, gold, aluminium, nickel, and platinum.

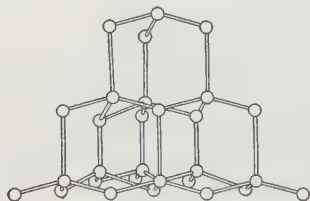


FIG. 29.

(3) **The Cube-centered Lattice** (Fig. 28). This type is represented by sodium, potassium, iron, chromium, and tungsten.

There are, of course, other lattice types, some of which are complex. Thus, X-ray analysis shows that the diamond consists of carbon atoms arranged as in Fig. 29. The carbon atoms form tetrahedra, with four atoms at the corners of a tetrahedron and a fifth atom at the mass-center.

Figure 30 shows what is believed to be the atomic structure of calcite, silicon dioxide, zinc sulfide, copper, magnesium, and iron

EXERCISES

1. Show that the standard atmospheric pressure per sq. cm. is 1033.2 g.
2. 35.5 cc. of nitrogen are collected at 740 mm. What would the volume be at 760 mm.? What would it be at 755 mm.? at 765 mm.?
3. 12.3 cc. of oxygen are collected at 22° C. Find the volume at 0° C. What would it be at 32° C.?

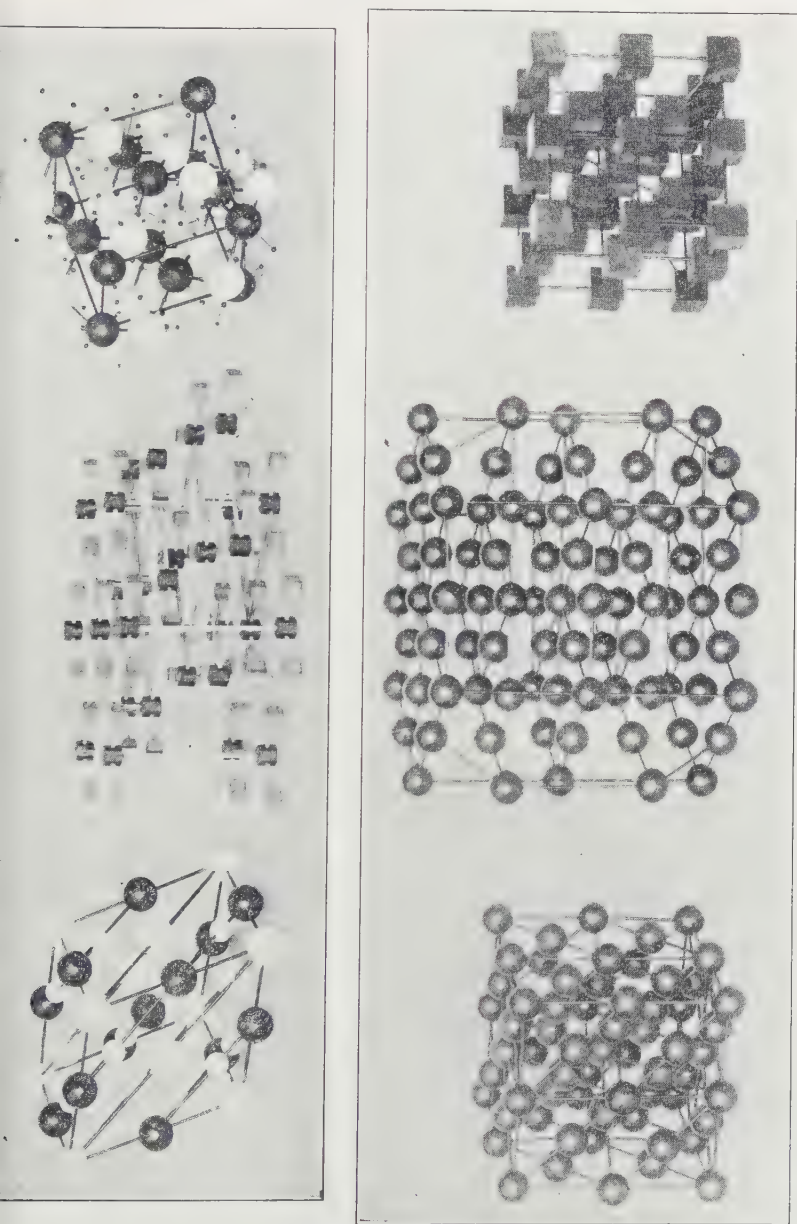


Fig. 30. Representation of Crystalline Structure of Calcite, Silicon Dioxide, Copper, Magnesium, and Iron.
Courtesy, General Electric Co.

4. Reduce 30 cc. of hydrogen at 80° F. and 775 mm. to S.T.P.; also to -10° F. and 756 mm.

5. Reduce 21.5 cc. of nitrogen, measured over water at 22° and 780 mm., to the dry condition and to S.T.P.

6. 1 liter of pure dry oxygen, at S.T.P., weighs 1.429 g. 650 cc. of this gas, measured over water at 18° C. and 755 mm., will contain what weight of the dry gas?

7. The density of a certain gas referred to air is 1.53. Making use of the data contained in the Appendix, find the sp. gr. of the gas referred to oxygen and to hydrogen.

8. Suppose the volume of a flask is 200 cc. and that it holds 0.2625 g. of oxygen, measured at 17° and 742 mm. From these data find the density of oxygen at S.T.P.

9. A quantity of gas has a volume of 30 cc. at 25° C. At what temperature, the pressure remaining constant, would its volume become 50 cc.?

10. The result of a calculation gave 22.4 liters of a gas at S.T.P. The gas was collected over water at 20° and under pressure of 750 mm. Find its observed volume.

11. When a gas is collected over mercury at ordinary temperatures, is it necessary to correct for the vapor of mercury? Explain.

12. Outline the kinetic-molecular theory of matter.

13. State four different laws of gases and show that they are explained by the kinetic theory.

14. State some conspicuous exceptions to the laws of Boyle and of Charles. Explain these exceptions in terms of the kinetic theory.

15. Explain evaporation and diffusion in terms of the kinetic theory.

16. How do the molecular relations in a liquid differ from those in a solid? What evidence can you give to show that the molecules of gases and liquids really move?

17. The mean speed of hydrogen molecules, at S.T.P., is 1,859 meters. Account for the fact that hydrogen diffuses through the air at a much lower rate than this.

18. Compare numerically the diffusibilities of the following pairs of gases: (a) H_2 and CO_2 ; (b) N_2 and NH_3 ; (c) CH_4 and HCl .

19. What do you understand by the partial pressure of a gas? State Dalton's law of partial pressures.

20. Why does a gas give out heat when compressed, and suffer a drop in temperature when allowed suddenly to expand through a small orifice?

21. What is the difference between amorphous and crystalline substances? Define the term crystal.

22. What is known about the exterior of crystal form, and of what value is it?

23. How have scientists learned something about the interior arrangement of the particles of crystals? Illustrate.

24. Outline one method for obtaining X-ray spectra.

25. What is the difference, if any, between the nature of X-rays and of ordinary light rays? How are X-rays produced? Who first suggested the possibility of using crystals as X-ray gratings?

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CHAPTER IV

THE RADIOACTIVE ELEMENTS

65. **Historical.** — The discovery of radium is one of the most important and brilliant in the history of the world, for it has created a new science, namely, **radioactivity**.

When a glass tube containing air or other gas is exhausted by means of an air-pump until the pressure is only a very small fraction of a millimeter, the tube is known as a vacuum tube. When a high-voltage electric current is passed through such a tube, very small negative particles — electrons — emanate from the cathode at high velocity. These are known as **cathode rays**, and were discovered by W. Crookes, in 1878. The negative electrons constituting the cathode rays move in straight lines, and when they strike the surface of the tube or the surface of another body placed athwart their path, a fluorescence is produced (Fig. 24). With lead glass, for example, the glow is bluish.

In 1895 W. C. Roentgen discovered that the radiation produced outside an ordinary cathode tube has great penetrating power, being able to pass through bodies of considerable thickness. These **Roentgen rays**, or **X-rays**, were found to produce photo-

graphic action similar to light; but X-ray photographs may be taken without removing the cover of the plate holder. The rays are produced when the anode of a vacuum tube is employed as a target for the cathode discharge, *i.e.*, when it is bombarded with electrons.

In 1896 the French physicist, H. Becquerel, discovered that minerals containing uranium, gave off rays which were capable

- (1) of penetrating black paper and affecting the photographic plate;
- (2) producing fluorescence in certain substances (zinc sulfide and barium platinocyanide);
- (3) “ionizing” air and other gases and discharging an electroscope (Fig. 31);
- and (4) passing through

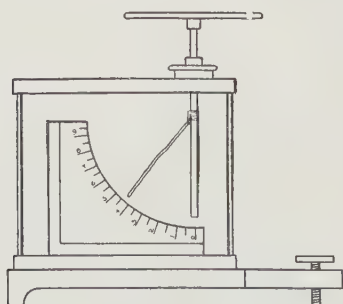


FIG. 31.



SIR WILLIAM CROOKES (1832-1919).



MARIE SKŁODOWSKA CURIE (1867-).

plates of metal. These rays were called 'Becquerel rays'; they are similar to X-rays in many of their properties. About two years later, it was also discovered that thorium and its compounds possess properties similar to those of uranium and its compounds, and the name "radioactivity" was applied to these extraordinary properties.

Soon after the discovery of this new radiation, Madame Curie, working in conjunction with her husband, the late Professor Curie, of Paris, made the following generalization:

Radioactivity is a property of the atom. It is not affected at all by the nature of the chemical combination in which the atom exists, nor by the physical conditions.

In 1897 the Curies worked on pitchblende residues [Pitchblende occurs in Bohemia; it contains the oxide, U_3O_8 , as well as impurities.] from which practically all the uranium had been extracted, and found that they were radioactive. They were led to suspect the presence of a new element in pitchblende more radioactive than uranium; indeed, they soon discovered a radioelement which was named **polonium**. It was found associated in small quantity with the bismuth extracted from the pitchblende.

Something like a ton of the residues was separated into different components, and it was discovered that the barium sulfate obtained was quite radioactive. By treating the barium sulfate, a small quantity of a new compound was prepared which was at least 1,000,000 times as active as uranium. The compound was radium bromide. They termed the new element, which was very radioactive, **radium**. The spectrum, general chemical relations, and atomic weight of the element showed it to be a member of the alkaline earth family.

Madame Curie succeeded in preparing pure radium chloride in 1902 and in isolating radium in 1910. Radium chloride was subjected to electrolysis, a mercury cathode being employed. The radium amalgam was placed in an iron boat, and the latter heated in a silica tube while a current of hydrogen under reduced pressure was being passed through. The mercury volatilized, leaving the radium behind as a white shining metal. Radium melts at 700° , loses its luster in air, and interacts vigorously with water to form hydrogen. It is very similar to barium, but is somewhat more reactive. Radium compounds are similar to barium compounds, but are in general less soluble in water. They impart a carmine tint to the Bunsen flame.

Numerous radioactive elements have been discovered, the total

number being approximately forty. Many radio-elements, such as uranium and radium, occur in 'uranium ores'; while others, such as thorium and mesothorium, are constituents of 'thorium ores.'

66. **The Nature of the Radiations.** — Radioactive substances emit three principal types of radiation, namely, the *alpha* (α), the *beta* (β), and the *gamma* (γ). The three types of 'rays' affect the photographic plate, cause certain fluorescent substances to glow, and 'ionize' the air and other gases. These effects are used in the detection and measurement of the different types of radiation.

(1) **Alpha Rays.** These rays are positively charged atoms of helium (He^{++}), or helium atoms each minus two electrons, which move with approximately one-tenth of the velocity of light (30,000 kilometers per second). They can be detected by means of the Crookes **spinhthariscopes** (Greek, *spark + to view*). A minute quantity of a radium compound is placed in front of a screen covered with zinc sulfide (Fig. 32).



FIG. 32.

When the helium particles strike the zinc sulfide, flashes of light are produced, which are magnified by means of a lens. By resting the eye in a dark room for 15 to 20 minutes, the flashes may be seen. The alpha rays are feebly penetrating, nearly all being stopped by a sheet of paper, or by a sheet of aluminium 0.1 mm. thick. The alpha rays, being positively charged, are affected by a magnetic field, as shown in Fig. 33, but are deviated in the opposite sense to the beta rays. The deviation is slight, however, for the mass is great as compared with that of the beta rays. The alpha particle possesses a mass about four times that of the hydrogen atom.

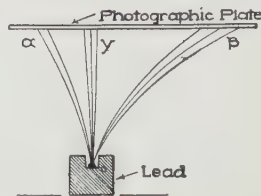


FIG. 33.

(2) **Beta Rays.** These rays are identical with cathode rays, *i.e.*, they are electrons, or free atoms of negative electricity. It is of interest to know that Johnstone Stoney first suggested, in 1891, the word electron as a name for the natural unit of electricity. The velocity of beta particles varies in different cases, the maximum being nearly as great as that of light (300,000 kilometers per second). They have greater penetrating power than alpha particles, but are virtually stopped by a sheet of aluminium 1 cm.

thick. These rays are greatly deviated by a magnetic field (Fig. 33), and also ionize the air, producing fog-tracks, which are fainter than those of the alpha rays. The mass of the electron is very small, being about $1/1845$ of the hydrogen atom.¹

(3) **Gamma Rays.** These rays are very similar to X-rays (65); that is, it is believed that they are light waves, the wave-length being much less than that of visible light. The gamma rays have great penetrating power, being able to penetrate relatively thick layers of metals. They are not deviated by a magnetic field (Fig. 33).

When the alpha particles pass through the air-molecules, the molecules of air suffer ionization, and the ionized particles serve as nuclei on which moisture may condense. By placing a particle of radium in a flask containing air saturated with moisture and then cooling the air quickly by expansion, lines of fog are produced. These fog-tracks, when powerfully illuminated, may be photographed (C. T. R. Wilson). The accompanying plate ("Fog-Tracks from Radium") shows alpha rays from radium and radium emanation. Electrons, also, produce fog-tracks.

67. **Spontaneous Disintegration of Atoms.**—There are, as previously stated, about forty known radioactive elements, all of which are derived from natural minerals containing either uranium or thorium, the two elements with the highest atomic weights, and both of which were known when Becquerel discovered radioactivity. Rutherford not only showed by his researches that radioactive substances give out three distinct types of radiation, but in 1902–03 he advanced the theory that the process of radioactive change is the result of a **spontaneous disintegration** on the part of the radioactive elements, in consequence of which new elements are produced. These new elements are frequently less stable than are the parent elements, and decompose, producing other elements, the process continuing through many stages until a final, stable disintegration product is produced, which appears to be a form of lead.

It is held that the spontaneous disintegration of radioactive elements is independent of conditions and the nature of combination in which the atom exists, that it goes on at a definite rate despite all the chemist is able to do. Radioactivity is, then, a property of the atom, the atoms of the two parent elements, uranium and thorium, undergoing spontaneous disintegration,

¹ Theoretically, the mass of the electron at the velocity of light would be infinite.

producing elements with lower atomic weights. These radioactive changes may be divided into two types:

(1) **The alpha-ray change.** *The atom of the element, such as uranium, loses a particle of mass 4 carrying two positive charges, i.e., the nucleus of the helium atom (He^{++}).*

(2) **The beta-ray change.** *The particle shot off is an electron; its mass is therefore negligible and it carries a single negative charge.*

When an alpha-ray change takes place, therefore, the atom loses 4 units in weight; and when a beta change occurs the weight of the atom is virtually unaltered, since it requires over 1,800 electrons to possess the mass of one atom of hydrogen.

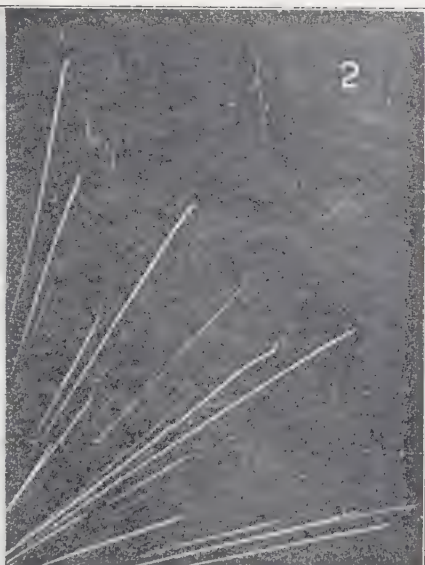
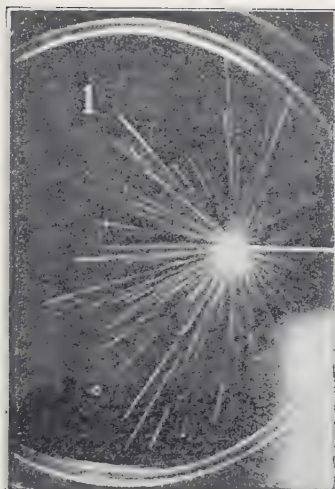
The theory of the spontaneous decomposition of radioactive elements is generally accepted. The researches of many investigators, particularly those of Rutherford and of Soddy, have placed the theory upon a firm foundation.

The **rate of change** or **period of average life** of a radioactive element is its most important property. As a result of calculations based upon experimental data, it has been possible to determine the rate of change or the period of average life of radioactive elements. According to F. Soddy, the period of average life is the sum of the separate periods of future existence of all the individual atoms divided by the number in existence at the starting-point. The following illustration is given by Cameron:

"If a church, at a fixed time, contains a number of people of different ages, then, given the number of years each person will live after leaving the church, the average life of the congregation is reckoned from the time fixed by the church attendance."

The periods of the average life of the radio-elements vary greatly. The average life of radium is about 2,500 years. This means that if a mass of radium, say, one gram, were set aside, at the end of one year $1/2500$ th of the radium would have changed or disintegrated. The average life of uranium is very long, namely, 8×10^9 years, or 8,000,000,000 years.

The time-period of a radioactive element is usually taken as the time required for the element to be half transformed. For radium this period is about 1,600 years, which means that if one gram of radium were set aside, half of it would be unchanged 1,600 years from now. To put it another way, if a gram of radium had been set aside at the beginning of the Christian era, nearly half of it would still be in existence. This slow disintegration of radium is a very valuable property. As expressed by M. A. Evans: "The practical importance of radium depends wholly on its radio-



FOG-TRACKS FROM RADIUM (C. T. R. WILSON).

1, 2. Paths of helium atoms

3. Part of 2, enlarged.

4. Paths of electrons.

activity. It is sometimes asked why radium possesses a greater importance than other radioactive elements. The principal reason is that radium has a period of half-change long enough to be regarded as a practically permanent source of radioactivity, but, at the same time, short enough to render it a highly active and concentrated source."

Starting with uranium (atomic weight approximately 238), the following table shows the different elements produced as the result of successive spontaneous disintegrations in the uranium-radium-lead series. When an alpha (helium) particle is expelled, the fact is indicated by the symbol He, and when an electron is lost, the symbol E is employed.

URANIUM-RADIUM DISINTEGRATION SERIES

(Y = years, D = days, M = minutes, S = seconds)

Element	Symbol	At. Wt.	At. No.	Particle Ejected	Period of Half-change
Uranium I.....	U ₁	238	92	He	5×10^9 Y
↓					
Uranium X ₁ ...	UX ₁	234	90	E	24.6 D
↓					
Uranium X ₂ ...	UX ₂	234	91	E	1.15 M
↓					
Uranium II....	U ₂	234	92	He	2×10^6 Y
↓					
Ionium.....	Io	230	90	He	6.9×10^5 Y
↓					
Radium.....	Ra	226	88	He	1580 Y
↓					
Radon.....	Rn	222	86	He	3.85 D
↓					
Radium A.....	RaA	218	84	He	3.0 M
↓					
Radium B.....	RaB	214	82	E	26.8 M
↓					
Radium C.....	RaC	214	83	E	19.5 M
↓					
Radium C ₁	RaC ₁	214	84	He	10^{-6} S
↓					
Radium D.....	RaD	210	82	E	16.5 Y
↓					
Radium E.....	RaE	210	83	E	5.0 D
↓					
Radium F..... (Polonium)	RaF or Po	210	84	He	136.0 D
↓					
Radium G..... (Radio-lead)	RaG or Pb	206.0	82

(He = Helium Atom and E = Electron)

In passing from radium to lead, there is a loss of 5 helium atoms ($5 \times 4 = 20$), which means that the atomic weight of the lead of the uranium-radium series should be 206 (226-20). Ordinary lead, from non-radioactive sources, has an atomic weight of 207.22. In 1913, Soddy suggested that lead derived from minerals containing uranium might have a lower atomic weight. T. W. Richards determined the atomic weight of lead in a very pure specimen of uranio-lead from Norwegian cleveite and found it to be 206.08, a number in striking agreement with the theory of Rutherford. This atomic weight of lead has been confirmed by other investigators. According to Richards, ordinary lead has a density of 11.337, while that of uranio-lead is 11.273, — a difference of 0.56 per cent.

It was shown by Ramsay that radium emanation (372) belongs to the family of rare gases; it was renamed *niton*, but is now called *radon*.

It should be added that uranium II can disintegrate by shooting off an alpha particle in two different ways: (1) in the transformation given above it appears that about 92 per cent of the atoms of uranium II suffer an alpha-ray change, passing into ionium, and that ionium is then transformed into radium, etc.; and (2) that 8 per cent of the atoms of uranium II appear to form uranium Y, which is regarded as the parent substance of the actinium series, of which a form of lead is the final product. In other words, the actinium series appears to be a branch of the main chain of the uranium-radium-lead transformation.

68. Other Disintegration Series. — Thorium (atomic weight, 232.15), like uranium, is the starting-point of another series of radio-elements, the end product of which appears to be a form of lead. The theory is advanced that the thorium atom loses 6 helium atoms during its transformation into lead, which would give this form of the metal an atomic weight of approximately 208 ($232 - 4 \times 6 = 208$). An atomic weight determination of lead from Norwegian thorite was made by Hönigschmid, and found to be 207.9, a number in close agreement with the theoretical value, namely, 208.

We see, therefore, that there are forms of lead which differ in mass or in atomic weight. Forms of an element which have slightly different atomic weights but identical chemical properties are called **isotopes** (Greek, meaning *equal + place*). They occupy the same place in the periodic table (81) and have the same atomic number (86). By referring to the table showing the disintegration of uranium it may be seen that RaB, RaD, and

RaG (radio-lead) are isotopes. The chief radio-elements are uranium, radium, actinium, and thorium.

69. "**The Displacement Law.**" — The relation between the position of a radioactive element in the periodic table (Chap. V) and the radiation expelled by the element producing it may be expressed as follows:

(1) *The emission of an α -particle by an element results in the production of an element having an atomic number diminished by 2, that is, it occupies a position in the periodic system two places lower down than does the parent element.*

(2) *When the disintegrating element emits a β -particle, its atomic number is increased by 1, that is, the product occupies a position one place higher than does the parent element.*

This is known as the "displacement law."

Uranium I has the atomic number of 92, while Uranium X_1 and Uranium X_2 have atomic numbers respectively of 90 and 91. Uranium II has the atomic number of 92 and is therefore an isotope of Uranium I. (See Fig. 34.)

70. **Counting the Atoms.** — When radon (372) or some other element capable of furnishing α -rays is sealed up in a glass tube the walls of which are less than 0.01 mm. thick, it is found that α -particles pass through the tube. By enclosing this tube in a wider evacuated tube having sealed-off ends and thick walls, one can no longer detect α -particles outside the tube. The particles must have been retained, therefore, in the space between the tubes, or in the walls of the outer tube. By means of spectroscopic tests helium has been found in the evacuated space between the tubes, showing that α -particles are helium atoms, each atom carrying two positive charges (He^{++}). *Experiment has shown that 1 g. of radium in one year produces 167 cubic millimeters (0.167 cc.) of helium.*

When a radioactive element emits an α -particle, each particle produces a flash of light if allowed to strike a screen coated with zinc sulfide (66).

It appears, then, that each disintegrating atom in a radioactive transformation yields one α -particle, and consequently one helium atom. This important conclusion was established by *counting experiments*. In these experiments the number of atoms disintegrating in a given time was known, and the number of α -particles given off in the same time was determined: for example, by counting the scintillations produced by the incidence of every single α -particle upon the zinc sulfide screen.

According to another method the number of particles (molecules) present in 1 cc. of every gas (S.T.P.) is $2.71 \cdot 10^{19}$. Theoretically, therefore, 167 cubic millimeters of helium should contain $2.71 \cdot 10^{19} \times 0.167 = 4.53 \cdot 10^{18}$ atoms (molecules), a number in excellent agreement with the one found before. We thus have very convincing proof of the atomistic conception of matter, for we are really able to count the number of particles occupying a given volume of a gas. (See Avogadro's Constant, 189.)

71. Atomic Energy. — When a compound of radium, for instance the bromide, disintegrates, a great deal of energy is liberated continually as heat. The radium compound is warmer than the surrounding atmosphere. The amount of energy stored in the nuclei of atoms is of a higher order of magnitude altogether than that generated by any known chemical reaction, such as the combustion of fuel or the oxidation of aluminium or phosphorus. One gram of radium evolves about 137 calories per hour, and the total heat available is over 2,000,000,000 calories per gram. When a gram of carbon burns to CO_2 , about 8,000 calories are evolved. One gram of radium therefore evolves hourly heat more than enough to raise its own weight of water from the freezing point to the boiling point; while in ten years the energy set free by one gram of radium equals that developed in the burning of over a thousand grams of carbon. It is indeed marvelous that radium keeps pouring out this enormous quantity of energy year after year without sign of abatement. Man has no control over the process. He can only look on and wonder. "There is no way of turning the steam on and off as it is wanted."

Soddy says: "The primary source of natural energy, by virtue of which the universe keeps going over immense periods of time, are to be sought not in the great masses of glowing matter dotted about the heavens, nor in their motions under the action of gravity, nor in any of the grosser relations between energy and matter in bulk, but in the individual atoms of which it is made up."

72. Effects Produced by Radium. — Radium (or a compound of radium) decomposes water. It is therefore dangerous to seal up radium or other highly radioactive substances, either in solution, or in an imperfectly dried condition, for indefinite periods, for the gases formed might burst the containing vessel. The radiations also have a coloring action on common glass and on many gems and minerals. Ordinary glass is usually colored violet or purple, but sometimes brown. The rays produce fluorescence in many substances: *e.g.*, zinc sulfide, barium platinocyanide, and

the diamond. Again, they sterilize seeds and destroy micro-organisms.

Radium is employed in the treatment of cancer and allied diseases. It is announced that it is a cure for certain types of cancer, being of great value in the treatment of skin, lip, tongue, and tonsil cancers; it is also an important aid in surgery, and serves as a palliative in certain incurable diseases. Radium has been applied with success to chronic infected wounds, and has aided in the treatment of scars.

The alpha rays are feebly penetrating, and are but little used. Beta radiation is always employed in conjunction with gamma radiation. Beta radiation is used for superficial conditions, and the gamma radiation in this case may probably be ignored. Gamma radiation is employed when deep penetration is required. One of the chief objects in the employment of radium is to get the effect of the deeply penetrating gamma rays.

In the application of radium it must be borne in mind that its rays may produce sores, for they have a tendency to kill the cells of the skin. Radium is continually producing emanation, which may be used instead of radium itself in the treatment of disease. The emanation is pumped off from time to time, collected in tiny glass tubes, and then inserted in the flesh near the cancer or similar growth. The emanation breaks down, producing the "rays," which act on the diseased tissue.

73. The Significance of Radium. — The discovery of radioactivity has thrown a great deal of light upon the structure of matter. We no longer regard atoms and molecules as imaginary particles, but as being real. In fact, we are now able to count the charged atoms (or monatomic molecules) of helium as they produce flashes of light on the zinc sulfide screen or enter the electroscope. Moreover, scientists have arrived at the conclusion that an atom has a positive nucleus surrounded by electrons. In other words, we have atomic systems, those of the radioelements being unstable. Thus, it is estimated that one gram of radium is continuously shooting off helium particles at the rate of many billions per second, with speeds which reach 12,000 miles per second. These atoms are now being employed in the bombardment of other atoms, and this has led to artificial transmutation (93). Scientists have also reached the conclusion that an atom is largely a vacuum, for the diameter of the nucleus is exceedingly small as compared with the dimensions of the atom as a whole. The diameter of the positive nucleus of the hydrogen atom is

estimated to be about $1/1845$ that of an electron. The dimensions of the atom and its parts are estimated to be as follows:

Diameter.

Atom.....	$2 - 4 \times 10^{-8}$ cm.
Electron.....	1.88×10^{-13} "
Proton.....	1×10^{-16} "
Nucleus (not hydrogen).....	$3 - 30 \times 10^{-13}$ "

When the diameter of the proton is multiplied by 10^{13} , the size of the particle becomes 0.01 mm. A particle of this size is barely visible to the unaided eye.

An atom is largely empty space. The proton has a density of 10^{24} , while that of the electron is 10^{11} , both being referred to water taken as unity.

Some one has estimated that if all of the protons and electrons in the body of an average man could be brought close together, they would occupy less than one millionth of a cubic millimeter (58).

The significance of radium with respect to energy has already been considered (71). For years the astronomer has been at a loss to account for the enormous amounts of energy given out by the sun and stars. It is now suggested that the subatomic energies may be the source of the radiant energy of the sun.

Professor Joly has calculated that "if there are two parts of radioactive material for every million million parts of other matter throughout the whole of the earth, and this is considerably less than he has found on the average in the earth's crust, then this earth, instead of cooling off, is actually heating up."

Radioactive changes appear to offer a means of estimating certain periods of time. A mineral is examined to determine the amount of uranium, lead, and helium present. Thus, one gram of uranium gives off helium at the rate of 1 cc. in 16,000,000 years. Samples of the mineral fergusonite contain 26 cc. of accumulated helium gas per gram of uranium; hence it is concluded that the samples of this mineral are at least 416,000,000 years old. Some of the helium may leak out, since it is a gas. There are also other complications.

74. The Sources and Production of Radium. — It has been stated that uranium is the parent element from which radium is produced. Radium is found, therefore, in all ores of uranium, and in no others. Furthermore, the ratio between the radium present and the uranium is, in general, fairly constant, amounting to about 1 part of radium to 3,000,000 parts of uranium. This

means that after uranium has been producing radium for a sufficient time the system comes to radioactive equilibrium, with about 3,000,000 times as much uranium as radium. This shows why the quantity of radium in existence is so small, and why it is so expensive to prepare it from uranium minerals. To illustrate, there are about 3 tons of uranium per gram of radium. The average life of radium, as previously stated, is estimated to be about 2,500 years, while that of uranium is about 8,000,000,000 years!

In Europe radium has been produced in considerable quantity from **pitchblende**, uranium oxide, U_3O_8 . There are a number of impurities in the mineral, and the preparation of the bromide or the chloride from it is a complicated process.

Radium has been produced in greater quantities in the United States from **carnotite** ($K_2O \cdot 2UO_3 \cdot V_2O_5 \cdot 3H_2O$), a light canary-yellow mineral, occurring chiefly in Colorado and Utah. This is a valuable ore, for it is worked for uranium and vanadium as well as radium. The total domestic production of radium up to 1921 was approximately 115 g. During the year 1920 nearly 31 g. of radium in the form of various salts were produced. One American chemical company alone produced in 6 years (1913–1918) 39 g. of radium, and up to the year 1922 its production is said to have been 72 g.

About 150 g. of radium have been produced in the United States from Colorado carnotite ore. In 1926 the total amount of radium in use in the whole world was not much above 240 g., or a little over half a pound.

Announcement was made in 1922 of the discovery of a radium ore in the Katanga district of the Belgian Congo. This ore is much richer in radium than the ores hitherto known, and it at once became the commercial source of the metal. While the ore is relatively rich in radium, the deposit does not appear to be a large one. The ore is refined in Belgium.

On May 25, 1921, Madame Curie was presented with a gram of radium at the National Museum in Washington. To secure this amount of the substance it was necessary to treat 500 tons of Colorado carnotite ore, containing 2 per cent of uranium. In 1 ton of pitchblende, containing 60 per cent of uranium, there is approximately 0.2 g. of radium.

Formerly, the price of radium usually varied from \$100,000 to \$125,000 per gram, but for several years the cost has been about \$70,000.

Radium is usually prepared as the bromide (RaBr_2) or the chloride (RaCl_2).

Not only is radium sold to hospitals and physicians, but it has been extensively used in the manufacture of luminous enamels or paints, a minute quantity of a radium salt being mixed with zinc sulfide. The principle involved in the luminescence of paint is the same as in the spinthariscopes; that is, zinc sulfide is bombarded by helium or alpha particles, light being produced. In the course of time the zinc sulfide is worn out, but the radium compound may be recovered and used again. Mesothorium, a disintegration product of thorium, is cheaper than radium and is luminous in the dark. It is now used on the faces of watches. Its average life is nearly 10 years and its half-value period is 6.7 years.

75. The Coolidge Cathode-Ray Tube.—It is of interest to note that W. D. Coolidge and his co-workers have developed a cathode-ray tube which can produce as many electrons per second as a ton of radium.

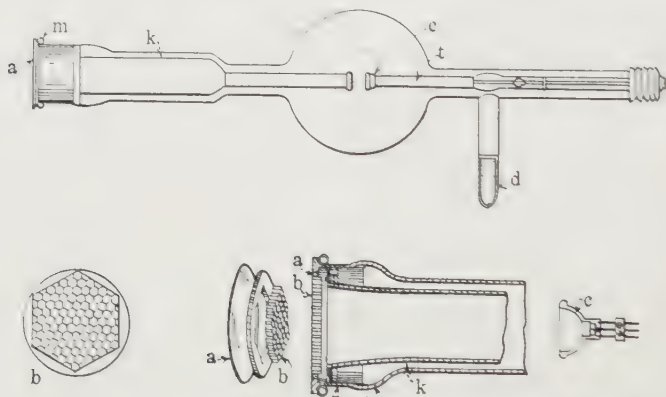
At one end of the Coolidge tube (Fig. 35) there is an anode "window," three inches in diameter, of nickel foil the thickness of which is measured in thousandths of an inch. A heated tungsten filament, originally employed by Coolidge in the X-ray tube and now known to all as an essential part of radio tubes, supplies the electrons. The glass tube is shielded by a copper tube so that the stream of electrons from the filament cannot strike the glass and cause punctures, thereby permitting operation of the tube at voltages far higher than heretofore.

Electrons are released by the heated tungsten filament at the relatively slow speed of one or two miles per second. Between the cathode and the anode—the window and the copper tube which serves as a shield—there is impressed upward to 350,000 volts of direct current. This accelerates the speed of the electrons to the average speed of 150,000 miles per second, depending upon the voltage, within the short space of about one inch between the cathode and the copper-tube shield. The electrons now coast the rest of the way through the highly evacuated tube and pass through the anode window, out into the air with but a slight diminution in speed. While the nickel window appears to be solid, it is really very porous, and the electrons in passing through it rarely hit a nickel atom despite the fact that there are about 500,000 layers of the nickel atoms. It is thus seen that the electrons fired off from radium move with greater speeds than do those so far produced with the Coolidge tube, but otherwise the two are alike.

The rays from the new cathode tube are so concentrated that many startling effects have been observed. When the tube is operated in a darkened room at 350,000 volts, a hum is heard and the window of the tube is surrounded by a ball of purplish light, about two feet in diameter. This glow results from the molecules of the gases of the air being ionized. Crystals of calcite or sticks of lime appear to become red-hot coals when exposed momentarily to the rays, but they are glowing with cold light; feldspar glows with a variety of rich colors; acetylene gas is transformed into a yellowish, insoluble solid;

and a rabbit's gray hair has been destroyed, to be replaced later by a profuse growth of longer, snow-white hair. The rays induce chemical change, and they will cause the death of small animals, such as mice. While the emanation has been referred to as a "death-ray," it could never be employed for an army at a distance, for the electrons do not travel far through air.

The new Coolidge tube will probably be a valuable instrument for scientific research, and it may be of importance in medicine.



Courtesy, General Electric Co.

FIG. 35. Explanation of Cathode-Ray Tube.

Upper: Diagram of tube.

Lower left: Construction of window.

Lower center: Details of window, shield and seal. Right: Section of cathode.

a. Anode window, a very thin piece of nickel foil through which the electrons pass into the air.

b. Window-support, a molybdenum hexagonal grid, to reinforce the window against the pressure of the atmosphere.

c. Hemispherical cathode cup, focusing the electrons released by the tungsten filament within the cup.

d. Charcoal trap for residual gases. When immersed in liquid air, the charcoal removes all traces of gas within tube.

k. Copper shield, preventing the electrons from striking the glass tube.

m. Water-cooling tube, to prevent the window from becoming heated.

r. Sleeve of invar, an alloy with about the same expansion as glass upon being heated. To this sleeve the anode is soldered.

s. Glass-to-invar seal.

t. Cathode shield.

According to a recent statement of Coolidge, a new form of his cathode-ray tube, by a method of cascading, has already been operated at 900,000 volts, three times as many as hitherto employed. By this new invention, it will be possible to enhance the power of the cathode-ray tubes and to speed up the electrons. Coolidge says:

"This opens a vista of alluring scientific possibilities. It has tantalized us for years to think that we could not produce in the laboratory just as high speed electrons as the highest velocity beta rays of radium and just as penetrating as the shortest wave-length gamma rays from radium. According to Sir Ernest Rutherford, we need only a little more than twice the voltage

which we have already employed to produce X-rays as penetrating as the most penetrating gamma rays from radium and three million volts to produce as high speed beta ray."

EXERCISES

1. Outline the various steps leading up to the discovery of radium.
2. Explain the meaning of the term radioactivity and radioactive element.
3. State the characteristics of the three types of radiation emitted when radium disintegrates.
4. Outline Rutherford's theory of the disintegration of atoms explaining the difference between the alpha-ray change and the beta-ray change. What is meant by the "average life" of a radioactive element? Also by the "half period"?
5. Outline the radioactive transformation of the uranium series, telling what you can about the properties of radium and of radon (actin).
6. Name the central elements of radioactivity, i.e. the radio elements which may be regarded as the source of all other radioactive elements.
7. What is meant by the isotopes of lead? What is the difference between the atomic weight of lead associated with uranium and that associated with thorium? Explain.
8. What is meant by atomic energy? Contrast the energy accompanying the disintegration of radium with that accompanying ordinary chemical change.
9. State some of the effects produced by radium. What is the meaning of the statement "radioactivity is a property of the atom"?
10. Outline the sources of radium. How may metallic radium be prepared? What other element does it most resemble?
11. What is the source of mesothorium? For what is it used?
12. Who discovered ionium? What is its relation to radium?

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CHAPTER V

CLASSIFICATION OF THE ELEMENTS. ATOMIC NUMBERS AND ATOMIC STRUCTURE

76. Metals and Non-metals. — The elements have long been classed as metals, or base-forming elements, and as non-metals, or acid-forming elements. This classification is far from ideal, for certain elements do not fall sharply into either class, *i.e.*, they possess both metallic and non-metallic characteristics, or are both basic and acidic in character: *e.g.*, arsenic and antimony. Such elements are sometimes called **metalloids**, or **amphoteric elements**.

Metals and non-metals do have certain general characteristics, however. Metals, *e.g.*, silver and gold, show what is known as a metallic luster; they are malleable, ductile, and are good conductors of electricity.

In general, the non-metals do not possess these characteristics. Metals, as a rule, have greater densities and higher melting points and boiling points than do the non-metals. There are conspicuous exceptions, however. The chemical differences will be discussed in a later chapter.

The metals may be divided into light and heavy metals, the light ones having a density less than five times that of water.

LIGHT METALS

The most useful and important light metals are as follows:

- (1) The Alkali Metals, — sodium and potassium.
- (2) The Alkaline Earth Metals, — calcium, strontium, and barium.
- (3) Beryllium and magnesium.
- (4) Aluminium.

HEAVY METALS

Of the heavy metals, gold, silver, copper, tin, lead, and iron have been longest known, owing to the fact that they occur free in nature, or can be easily prepared from certain of their com-

pounds called ores. Iron was perhaps the last of these metals to be prepared, for it is more difficult to liberate it from its compounds. Gold is found chiefly in the free state (native).

Bronze, an alloy of tin and copper, was used extensively by the ancients. Brass, essentially an alloy of copper and zinc, was also used by the ancients. Zinc, however, did not come into general use until comparatively recent times.

Other important heavy metals are: nickel, cobalt, manganese, chromium, tungsten, mercury (liquid), antimony, bismuth, and platinum and allied metals.

Gold and platinum and allied elements are called the *noble metals*.

NON-METALS

The elements usually classed as non-metals are as follows:

Hydrogen		Nitrogen		Helium	
Fluorine	the Halogens	Phosphorus	}	Neon	Inert gases
Chlorine		Arsenic		Argon	
Bromine				Krypton	
Iodine				Xenon	
		Boron		Radon	
Oxygen	}	Carbon	}		
Sulfur		Silicon			
Selenium					
Tellurium					

The elements in brackets constitute natural families. Hydrogen, oxygen, nitrogen, and the inert elements of the atmosphere are colorless, odorless, tasteless gases; chlorine and fluorine are greenish-yellow gases (fluorine is paler). Bromine, like the metal mercury, is a liquid at ordinary temperatures; it has a dark-red color and a very disagreeable odor.

77. Electropositive and Electronegative Elements. — The electrochemical theories of Davy and Berzelius were introduced in the beginning of the nineteenth century. According to the "dualistic system" of Berzelius, electric polarity was a property of the atoms of substances, and every compound consisted of two parts which were electrically different. Thus, barium oxide might be represented by the formula Ba^+O^- and carbonic acid gas by C^+O_2^- . The terms electropositive and electronegative are relative,

for an element may be electropositive toward one element and electronegative toward another. In general, it may be said that the metals and hydrogen are electropositive, while the non-metals are electronegative. The alkali metals are the most electropositive elements and fluorine the most electronegative.

78. Prout's Hypothesis. — In 1815–1816, Prout, an English physician, published papers in which he propounded the hypothesis that the atomic weights of the elements — taking that of hydrogen as unity — were multiples of hydrogen, the lightest element. This meant that all the atomic weights of elements were whole numbers, and that hydrogen was the primary form of matter, of which atoms of other elements were different aggregates. According to Prout, hydrogen corresponded to the protyle of the ancients. The hypothesis of Prout was found apparently to be untenable, for careful determinations of atomic weights by Berzelius, Dumas, Stas, and others proved that some of the atomic weights were not even approximate multiples of that of hydrogen: *e.g.*, that of chlorine is about 35.5. As we shall see later, Prout's hypothesis may have some foundation after all.

79. Döbereiner's Triads. — Between the years 1816 and 1829, J. W. Döbereiner noticed that certain closely related elements possessed atomic weights which exhibited a constant difference when arranged in sets of three, *i.e.*, the atomic weight of the middle element is approximately the mean of the other two. The following sets of elements illustrate Döbereiner's triads:

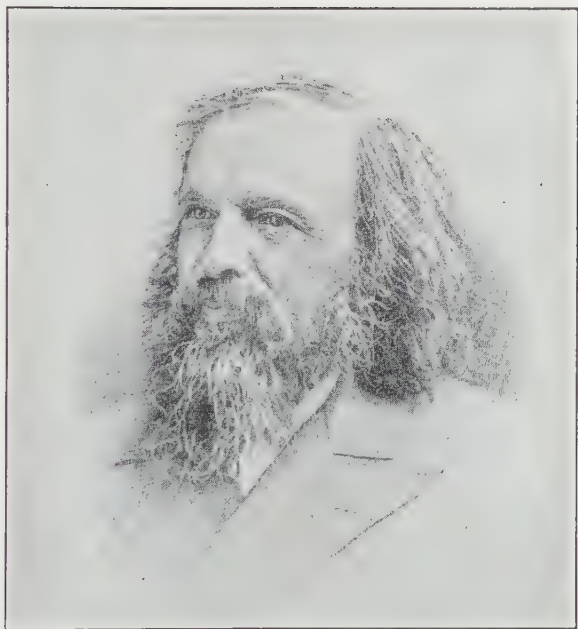
	<i>At. wts.</i>		<i>At. wts.</i>
Chlorine.....	35.46	Calcium.....	40.07
Bromine.....	79.92 (81.19)	Strontium.....	87.63 (88.72)
Iodine.....	126.93	Barium.....	137.37

The numbers in parentheses are the mean values of the two extremes.

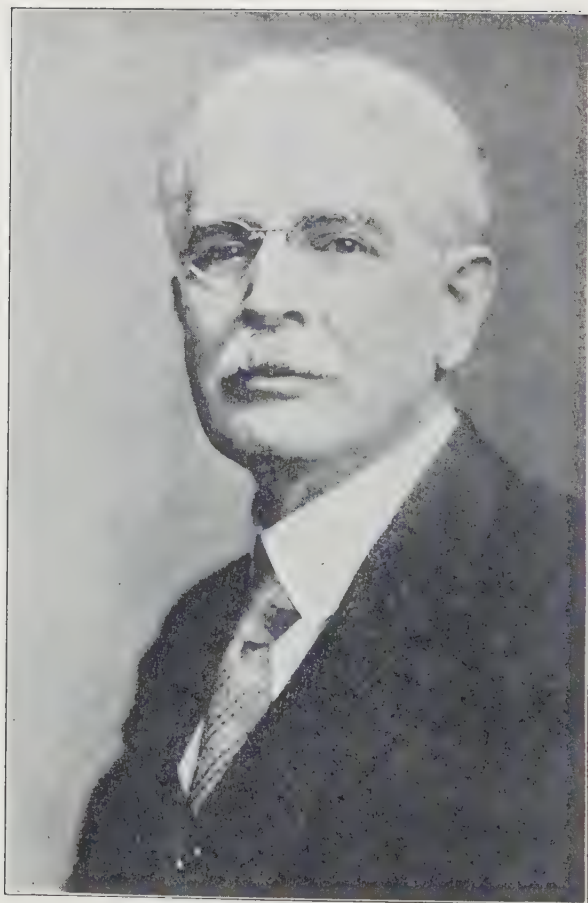
Furthermore, Döbereiner showed that certain closely related elements have atomic weights which are very nearly the same: *e.g.*, the triad Fe (55.84), Co (58.94), and Ni (58.69).

Döbereiner's observations did not lead far, but it was an attempt to arrange the elements according to their atomic weights.

80. Newlands' Law of Octaves. — J. A. R. Newlands (1863–1864) made an attempt to classify the elements according to their increasing atomic weights. He arranged a number of the elements according to the magnitudes of their atomic weights, and observed that, after the lapse of a certain period, the properties



DIMITRI IVANOWITCH MENDELÉEFF (1834-1907).



THEODORE WILLIAM RICHARDS (1868-1928).

of the elements now succeeding each other were similar to those of the previous group. To be more specific, he noticed that every eighth succeeding element was "a kind of repetition of the first"; that is, "**members of the same group of elements stand to each other in the same relation as the extremities of one or more octaves in music.**" Newlands termed this striking relationship the **law of octaves**.

The following periods of elements will serve as illustrations:

Li	Be	B	C	N	O	F
6.94	9	10.8	12	14	16	19
Na	Mg	Al	Si	P	S	Cl
23	24.3	27	28.1	31	32	35.5

According to this arrangement of the elements, sodium is the seventh element after lithium, and these metals have similar properties. In the same way magnesium is the seventh after beryllium, aluminium after boron, silicon after carbon, etc. These pairs of elements therefore have similar properties.

81. The Periodic System. — Soon after the publication of the classical papers by Newlands enunciating the Law of Octaves, D. I. Mendeléeff, of Russia, and Lothar Meyer, of Germany, independently made similar observations. In 1869, Mendeléeff communicated a paper to the Russian Chemical Society, entitled "On the Correlation of the Properties and Atomic Weights of the Elements." In this paper he presented his conclusions as to the "dependence between the properties and analogies of the elements on the one hand and their atomic weights on the other." In 1871, Mendeléeff published his first Periodic Table, in which the elements were divided into eight groups. In arranging the elements in groups, the atomic weight was considered to be the most fundamental property of the atom. When Mendeléeff arranged the elements according to their atomic weights, a repetition of properties was observed in the periods of the elements. We have a familiar illustration of this in the halogen family:

F (19), Cl (35.46), Br (79.92), I (126.93).

From 1894–1898, several new elements were discovered in the atmosphere. These are known as the *inert gases*, or the *Helium Family*. In modern tables of the periodic system these elements are placed in Group 0; therefore, including the eight groups in the earlier periodic tables, there are nine groups in all, — running from Group 0 to Group VIII, the last including closely related

elements arranged in triads and having atomic weights of nearly the same value (*e.g.*, Fe, Co, Ni). Hydrogen does not fit into the periodic system.

Omitting hydrogen, the elements are now arranged according to their atomic weights in nine groups, as shown in the table given below. The first short period contains 8 elements (He to F). The next element is Ne, which is similar to He, the one above it in the vertical column. In the same way, Na resembles Li, etc. The second short period ends with Cl, which is in the same group as F. We now come to the first long period, which contains 18 elements (A to Br). Three of these elements (Fe, Co, Ni) have similar properties, and atomic weights which are nearly of the same value, so they are placed in the last vertical column. These are sometimes called **transitional elements**. The second long period also contains 18 elements (Kr to I), the so-called transitional elements being ruthenium, rhodium, and palladium. These long periods are followed by other long periods, as may be seen by reference to the accompanying table. The long periods are divided into two series — an **even series** and an **odd series**.

The rare earth elements belong to the third long period, and osmium, iridium, and platinum are a trio of similar elements which have been assigned to Group VIII.

The last period of the table is a mere fragment, containing only seven elements, one of which (Number 87) is yet undiscovered. It is believed that this element is related to the alkali metals, and the name eka-caesium has been suggested for it. The first element in this period is radon (niton), a gaseous emanation of radium, and the last element is the metal uranium, which has the heaviest atom known.

The Groups of the elements from I to VII are divided into two Sub-groups or Families. Thus, in Group I we find the family of the alkali metals (Li, Na, K, Rb, Cs) and the copper family (Cu, Ag, and Au). The elements in the left vertical column belong to Sub-group A, while those in the right column belong to Sub-group B.

82. General Remarks on the Periodic System. — There are certain general relations in the periodic system:

(1) The valence of the atom of the element corresponds to the number of the group in which the element falls. Thus, helium has a valence of zero (no compounds of helium are known), sodium is univalent, calcium is bivalent, etc. Some elements, however, are multivalent: *e.g.*, chlorine has a minimum negative valence

PERIODIC TABLE*

Periods	Group 0	Group I	Group II	Group III	Group IV	Group V	Group VI	Group VII	Group VIII
Type of Oxide	—	R ₂ O RH	RO RH ₂	R ₂ O ₃ RH ₃	RO ₂ RH ₄	R ₂ O ₅ RH ₃	R ₂ O ₃ (RO ₂) RH ₂	R ₂ O ₇ RH	RO ₄ —
Type of Hydride	—	A B H 1 Li 3 1.008 6.94	A B Be 4 9.02	A B B 5 10.82	A B C 6 12.00	A B N 7 14.01	A B O 8 16.00	A B F 9 19.0	
First short period	He 2 4.002								
Second short period	Ne 10 20.183	Na 11 23	Mg 12 24.32	Al 13 26.97	Si 14 28.06	P 15 31.03	S 16 32.06	Cl 17 35.46	
First long period Even Series Odd Series	A 18 39.94	K 19 39.1	Ca 20 40.07	Sc 21 45.1	Ti 22 47.9	V 23 50.96	Cr 24 52.01	Mn 25 54.93	Fe 26 Co 27 Ni 28 55.84 58.94 58.69
		Cu 29 63.57	Zn 30 65.38	Ga 31 69.72	Ge 32 72.6	As 33 74.96	Se 34 79.2	Br 35 79.92	
Second long period Even Series Odd Series	Kr 36 82.9	Rb 37 85.44	Sr 38 87.63	Y 39 88.92	Zr 40 91.22	Cb 41 93.1	Mo 42 96.0	Ma 43 ?	Ru 44 Rh 45 Pd 46 101.7 102.91 106.7
		Ag 47 107.88	Cd 48 112.41	In 49 114.8	Sn 50 118.7	Sb 51 121.77	Te 52 127.5	I 53 126.93	
Third long period Even Series Odd Series	Xe 54 130.2	Cs 55 132.81	Ba 56 137.37	La 57 138.9	Ce 58 140.25				
The Rare Earth Elements. Atomic Numbers 59-71									
Fourth long period Even Series Odd Series		Au 79 197.2	Hg 80 200.61	Tl 81 204.39	Hf 72 178.6	Ta 73 181.5	W 74 184.0	Re 75 ?	Os 76 Ir 77 Pt 78 190.8 193.1 195.23
					Pb 82 207.22	Bi 83 209.0	Po 84	—85	
Fifth period	Rn 86 222	—87	Ra 88 225.95	Ac 89	Th 90 232.15	UX ₂ 91	U 92 238.17		

* The number at the right of the symbol is the Atomic Number of the element, and the number below is the Atomic Weight.

of 1 (HCl) and a positive maximum valence of 7 (Cl_2O_7). One valence, however, of the element corresponds to the group to which it is assigned.

(2) The valence of the element with respect to hydrogen increases regularly from Group I to Group IV, then decreases to Group VII (see Table).

With respect to oxygen, the valence increases regularly from Group I to Group VIII: *e.g.*, Na_2O , CaO , Al_2O_3 , CO_2 , P_2O_5 , SO_3 , Mn_2O_7 , OsO_4 .

(3) The formulae of the corresponding compounds of elements in the same group are analogous:

NaH	Na_2O	NaCl	NaOH	NaHCO_3	Na_2CO_3
KH	K_2O	KCl	KOH	KHCO_3	K_2CO_3

(4) The strongly basic elements are found in Groups I and II: *e.g.*, Na, K, Ca, Sr. In general, the elements in a family become more basic with increasing atomic weights. The elements which are strongly acidic (electronegative) in nature are on the right-hand side of the Table (Group VIII is excepted): *e.g.*, N, P, O, S, Cl, etc. Certain of the elements falling in the central groups are both basic and acidic (amphoteric) in character: *e.g.*, As, Sb, Al, Cr.

(5) The atomic weight of an element, according to Mendeléeff, conditions its properties. This is expressed by the **Periodic Law**:

The properties of the elements, as well as the constitution and properties of their compounds, are periodic functions of the atomic weights of the elements.

83. Applications of the Periodic Law. — Mendeléeff pointed out the following applications of the periodic system:

(1) **The classification of the elements.** Before the periodic system was developed, there was no comprehensive plan for the classification of the elements. By arranging them in groups and families the study of their physical and chemical properties is much simplified, and the memory is greatly aided. This is by far the most important application of the periodic law.

(2) **The prediction of new elements.** Mendeléeff stated in 1869 that the discovery of many yet unknown elements may be expected, and in 1871 he actually predicted the properties of three new elements which he called *Eka-aluminium*, *Eka-boron*, and *Eka-silicon* (from the Sanskrit, *Eka*, one). In less than twenty years confirmation of Mendeléeff's bold predictions was complete. *Eka-aluminium* was discovered by Lecoq de Bois-

baudran in 1875, and named *gallium* ($\text{Ga} = 69.7$); eka-boron was discovered by Nilson in 1879, and named *scandium* ($\text{Sc} = 45.1$) in honor of his country; eka-silicon was discovered by the German chemist Winkler in 1888, and appropriately called *germanium* ($\text{Ge} = 72.6$).

The striking way in which Mendeléeff's predictions were fulfilled is shown by the following illustration:

<i>Eka-silicon</i> <i>Predicted Properties</i>	<i>Germanium</i> <i>Observed Properties</i>
At. wt. 72, sp. gr. 5.5.	At. wt. 72.5, sp. gr. 5.46.
Oxide, EsO_2 , sp. gr. 4.7.	Oxide, GeO_2 , sp. gr. 4.7.
Chloride, EsCl_4 , liquid boiling slightly below 100° , sp. gr. 1.9.	Chloride, GeCl_4 , liquid boiling at 86° , sp. gr. 1.887.
Ethide, $\text{Es}(\text{C}_2\text{H}_5)_4$, liquid boiling at 160° , sp. gr. 0.96.	Ethide, $\text{Ge}(\text{C}_2\text{H}_5)_4$, liquid boiling at 160° , sp. gr. slightly less than that of water.
Fluoride, EsF_4 , not gaseous.	Fluoride, GeF_4 , $3\text{H}_2\text{O}$, white, solid mass.

(3) Estimation and correction of the atomic weights of elements.

In case of certain elements it is not possible to arrive at the atomic weights by the application of Avogadro's law. On account of practical difficulties, therefore, chemists were at one time in doubt as to the atomic weights of some of the elements. To illustrate, indium had an equivalent weight of about 38 and its valence was regarded as 2, so the atomic weight was thought to be 76. Arsenic has an atomic weight of 75, and it has properties very different from indium. Chemists reached the conclusion that indium has a valence of 3, and its accepted atomic weight is therefore 114.8 instead of 76. This places indium in the aluminum family (Group III) where it naturally belongs.

(4) The periodic system suggests problems for investigation.

The periodic law has suggested various problems for research in the field of inorganic chemistry: *e.g.*, tellurium has an atomic weight of 127.5, while that of iodine is 126.93, and should therefore precede tellurium in the table. The other properties of tellurium, however, place it in the sulfur family, and iodine belongs to the chlorine family. A number of most careful investigations have not reduced the atomic weight of tellurium below 127.5.

84. Some Defects in the Periodic System. — The periodic system is not perfect. In the first place, hydrogen is left without a place in the groups of the elements. Again, there are three exceptions to the arrangement of the elements in the order of

their atomic weights. We have just seen that tellurium precedes iodine, although the latter has the lower atomic weight. Argon (at. wt. 39.9) precedes potassium (at. wt. 39.1), and cobalt (at. wt. 58.94) precedes nickel (at. wt. 58.69). Furthermore, the atomic weights of the alkali metals place them in the same group as the metals of the copper family (Group I), yet gold is trivalent as well as univalent, and copper is usually bivalent. Some elements which appear to be chemically related are separated in the table: *e.g.*, copper and mercury.

Despite these imperfections, some fundamental relationship is undoubtedly represented in the periodic arrangement of the elements.

85. Relation of the Physical Properties of the Elements to their Atomic Weights. — The late T. W. Richards of Harvard devoted a great deal of attention to the determination of accurate atomic weights, which he used as a means to obtain a more fundamental knowledge of the properties of the elements. The relations of some of the physical properties of the elements to their atomic weights are exhibited in Fig. 36, in which the atomic weights are represented as abscissae and the physical properties as ordinates.

Curve I (at the top) represents the *reciprocals of the absolute melting points, i.e.*, 1 divided by the melting point on the absolute scale.

Curve II shows the *coefficients of expansion*.

Curve III represents the *atomic volumes, i.e.*, the volume of 1 gram-atomic weight of the solid element. Atomic volumes are obtained by dividing the atomic weights by the densities of the elements (22). Lothar Meyer prepared a curve of atomic volumes in 1870.

Curve IV (at bottom) shows the *compressibilities of the atoms*. According to Richards, the atoms themselves, as well as the spaces between them, are compressible. Note that the curves are wave-shaped, with the more fusible elements on the rising branches and maximal points, while the elements which have high melting points are on the descending branches at the minima.

86. Arrangement of Elements by Atomic Numbers. — We have seen that when cathode rays (streams of electrons) emanating from the cathode of a vacuum tube are suddenly stopped in their motion by striking a solid target (*e.g.*, platinum) placed at the anode, radiation from the anode occurs; that is, X-rays are produced (65). When different elements are employed as targets,

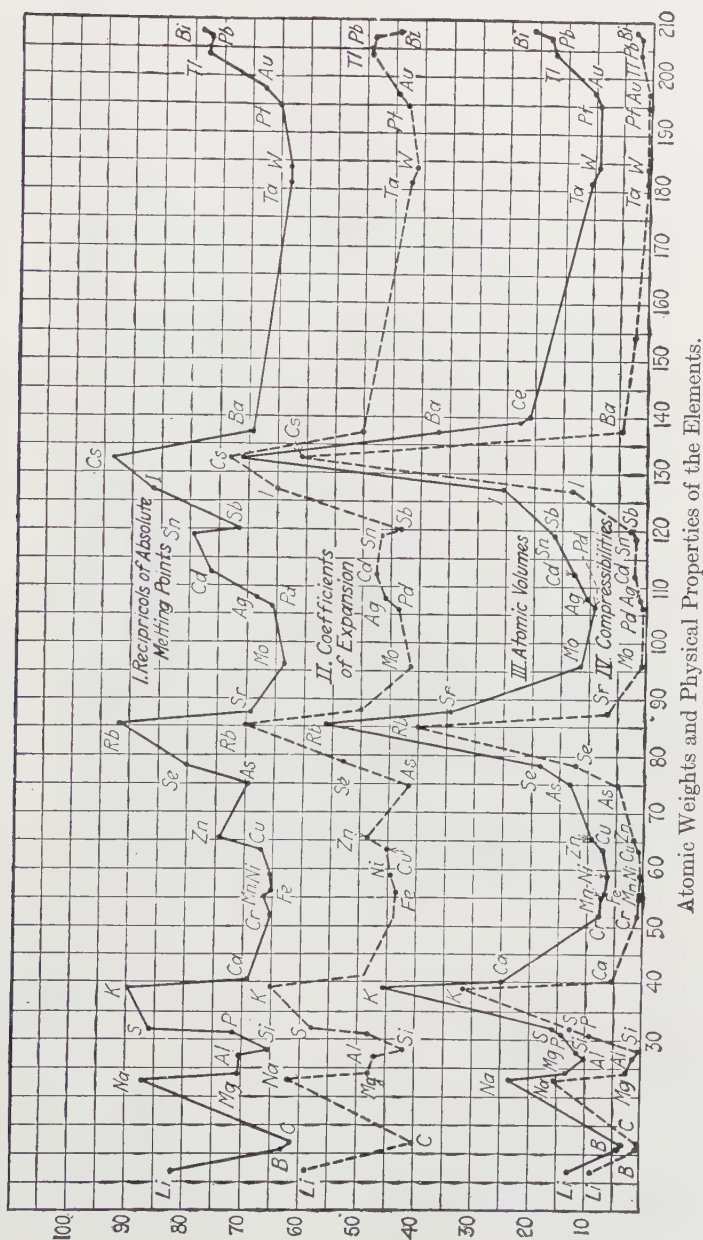
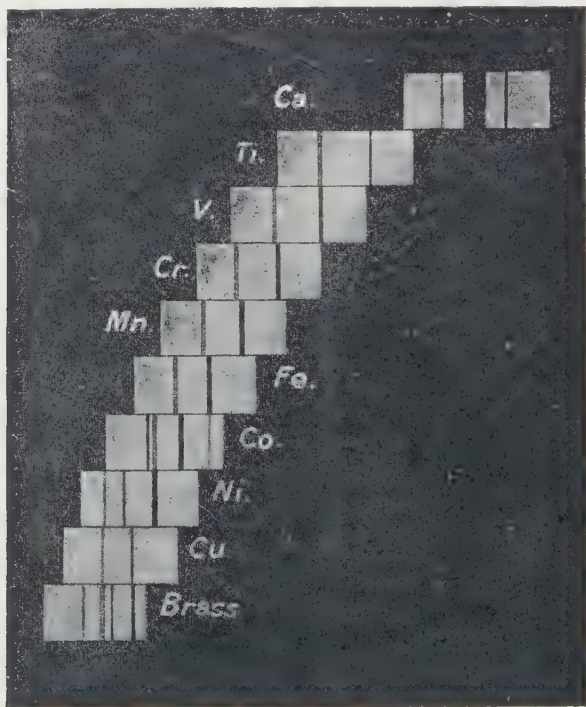


FIG. 36.

X-rays of slightly different wave-lengths are obtained and X-ray spectra are produced. Moseley, a brilliant young British physicist, who died fighting at Gallipoli in 1915, employed as targets the elements from aluminium to gold, and measured the wave-lengths of the X-rays produced (64). He observed that, the higher the atomic weight of the element the shorter the wave-length of the X-rays.



Courtesy, Macmillan and Co.

FIG. 37. X-Ray Spectra of the Elements from Calcium to Zinc (Moseley).

The spectrum of each element consists of two principal lines, but the cobalt-spectrum shows lines due to the presence of iron and nickel, the nickel appears to have contained some copper and the brass gives two lines due to copper and two lines due to zinc.

Furthermore, the shift was of the same magnitude in passing from element to element, say, from Al to Si and from Si to P. Other experimenters have confirmed and added to the facts discovered by Moseley. Whole numbers, called **atomic numbers**, have been assigned to the different elements. These numbers are to be found in the Periodic Table. Starting with hydrogen,

the atomic numbers run: H = 1, He = 2, Li = 3, Be = 4, B = 5, C = 6, etc., up to U = 92.

The X-ray spectra of the elements from Ca to Zn are shown in Fig. 37.

The elements may be arranged according to their atomic numbers as shown in the table below. It is similar to one recently proposed by von Antropoff. This table, with its device of connecting zones, has some advantages over the earlier tables. These advantages are admirably stated by A. A. Noyes,¹ as follows:

(1) All but three of the gaps have now been filled by the discoveries of new elements; most of which were made through studies of radioactivity and of the emission of X-rays.

0	I	II	III	IV	V	VI	VII										
He 2	Li 3	Be 4	B 5	C 6	N 7	O 8	F 9										
Ne 10	Na 11	Mg 12	Al 13	Si 14	P 15	S 16	Cl 17										
0	Ia	IIa	IIIa	IVa	Va	VIa	VIIa	VIII			Ib	IIb	IIIb	IVb	Vb	VIb	VIIb
Ar 18	K 19	Ca 20	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35
Kr 36	Rb 37	Sr 38	Y 39	Zr 40	Nb 41	Mo 42	43	Ru 44	Rh 45	Pd 46	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te 52	I 53
X 54	Cs 55	Ba 56	La-Lu 57-71	Hf 72	Ta 73	W 74	Re 75	Os 76	Ir 77	Pt 78	Au 79	Hg 80	Tl 81	Pb 82	Bi 83	Po 84	85
Rn 86	87	Ra 88	Ac 89	Th 90	Pa 91	U 92											

PERIODIC TABLE.

(2) The inverted position of the elements argon and potassium, cobalt and nickel, tellurium and iodine, is fully justified now that atomic-structure studies have shown that it is not the atomic weight, but another characteristic, the atomic number, that determines nearly all the properties of the elements.

(3) The rare earths still seem to be intruders; but this is only because the long period of 32 elements indicated by the structure of the atoms is, to avoid clumsiness, not shown in the table.

¹ *Science*, **69**, 1776, 21 (1929).

(4) The triplets now assume natural positions in the middle of the long periods; and form a continuous sequence with the next similar elements.

(5) There is now no break, but a progression, between these triplets and the succeeding elements, thus between nickel and copper, or platinum and gold.

(6) The relationships of the properties are much more fully indicated. Thus lithium and sodium are very closely connected with their nearest allies, potassium, rubidium, and cesium; and they are also connected, but only remotely, with their distant relatives, silver, copper, and gold. And the connecting zones lead directly from sulfur to selenium and tellurium, but only remotely to chromium, molybdenum, and tungsten.

When Moseley prepared the first chart of atomic numbers, there were several gaps, which indicated that new elements would be discovered. The missing elements corresponded to numbers 43, 61, 72, 75, 85, and 87; but all of these have been discovered with the exception of numbers 85 and 87.

The most recently discovered elements are:

Number	Name	Discoverer	Country	Year
72	Hafnium	Coster and Hevesy	Denmark	1923
43	Masurium	Noddack and Tacke	Germany	1925
75	Rhenium	{Noddack and Tacke		
	Bohemium	{Heyrovsky and Dobysek	Czecho-Slovakia	1925
61	Illinium	Hopkins	United States	1926

Druce and Loringhan have obtained a residue from manganese compounds which certainly contains element Number 75. Noddack reported in 1927 the preparation of pure rhenium. Number 85 is an unknown halogen ('eka-iodine'), and Number 87 is believed to be related to the alkali metals, being called 'eka-cesium.'

The atomic numbers are indicative of the physical and chemical properties of the elements, and they appear to be more fundamental than the atomic weights.

It is interesting to know that of the twenty elements constituting about 99.5 per cent of the earth's crust (18), those having even atomic numbers are not only more numerous than those having odd numbers, but they constitute more than 86 per cent of the whole. The great difference is due largely to the abundance of oxygen and silicon, both of which have even atomic num-

bers ($O = 8$, $Si = 14$). The most abundant metal (Al) has an odd atomic number, namely, 13.

ATOMIC STRUCTURE

87. The Rutherford-Bohr Atom. — In order to explain the disintegration of radioactive elements Sir Ernest Rutherford (1911), now of Cambridge University, propounded a bold theory concerning the structure of atoms. According to this theory, an atom has a nucleus which is positive, exceedingly small, and contains nearly the whole mass of the atom. Outside the nucleus there is a number of electrons corresponding to the atomic number of the atom. This number of electrons is exactly equal to the excess of protons in the nucleus. In general, a nucleus contains some electrons, and it is the number of positive charges (protons) of a nucleus in excess of the number of negative charges (electrons) which determines the atomic number of the element. An atomic system, therefore, consists of a nucleus and associated "planetary electrons," *i.e.*, electrons situated outside the nucleus. An atomic system may be either a normal atom or an ion. The electrons which encircle the nucleus are relatively far from it and from each other. We may obtain a rough picture of an atomic system by comparing it with our solar system, if we imagine the sun to be very small. The sun corresponds to the nucleus of an atom, and the planets to electrons outside the nucleus.

The ordinary chemical and physical properties of an atom are ascribed mainly to the configuration and motion of the outer electrons, while the mass and the radioactivity depend upon the structure of the nucleus. To illustrate, the hydrogen atom — the simplest atom — consists, it is believed, of one proton and one planetary electron, which revolves around the positive nucleus (Fig. 38). The atomic number of hydrogen is 1.

The helium atom consists of a nucleus containing 4 protons and 2 nuclear electrons, and of 2 planetary electrons (Fig. 39). The atomic number of helium is therefore 2. Such an arrangement of protons and electrons would appear to be very stable, and it is well known that helium is an inactive gas.

The lithium atom ($Li = 7$) has a nucleus consisting of 7 protons and 4 electrons, and it has 3 planetary electrons, 2 of which are assumed to be circulating in an inner orbit (Fig. 40). The positive valence of lithium is 1, corresponding to the outer planetary electron. When an atom of lithium loses an electron, it

passes into an ion (Li^+), as shown in the diagram. The atomic number of the element is 3, and its atomic weight is 7.

N. Bohr, in 1913, developed the theory of Rutherford and applied it to the explanation of the complicated optical spectrum of the atom. Under ordinary conditions Bohr assumes that the

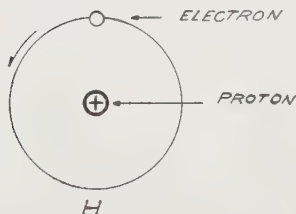


FIG. 38.

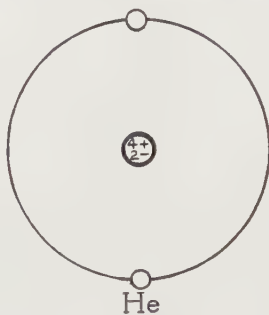


FIG. 39.

electron of the hydrogen atom rotates rapidly in a circular orbit relatively close to the nucleus; he also assumes that the single electron can move in a number of stable orbits, which are controlled by the attractive force of the nucleus. Now, in case the hydrogen atom is excited by an electric charge or otherwise, the electron may be displaced to another stable orbit where it cir-

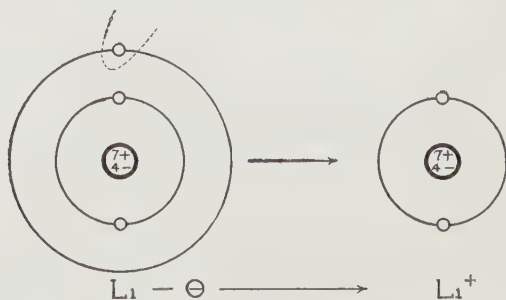


FIG. 40.

culates. It is furthermore assumed that the atom radiates only when the electron is transferred from one stable orbit to another of lower energy, *i.e.*, to an orbit closer to the nucleus. In a radiating gas giving the complete hydrogen spectrum, it is held that there are present many different kinds of hydrogen atoms, in

each of which the electron moves in one of the possible orbits demanded by theory.

The theory of Bohr assumes, therefore, that an atom emits light (radiates) only when the electron falls from one level to another,

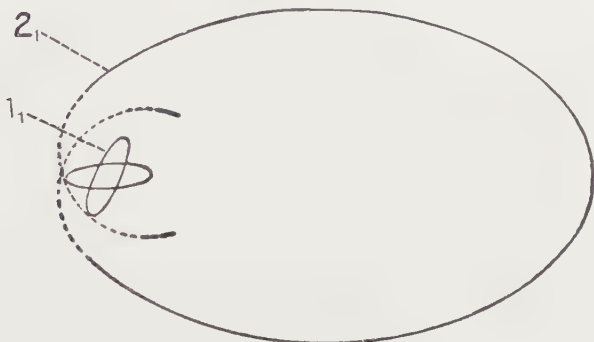


FIG. 41. Lithium (3).

or absorbs light only when the electron is raised from a lower to a higher level, *i.e.*, when it is displaced from a smaller to a larger orbit.

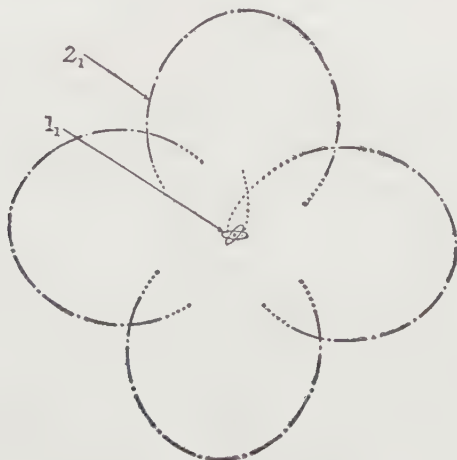


FIG. 42. Carbon (6).

In the Bohr atom it is assumed that the orbits of the electrons lie in different planes. The theory affords a satisfactory explanation of complex optical spectra and is also helpful in explaining

X-ray spectra. With increase in atomic weights, the Bohr atom becomes much more complicated. Models illustrative of the orbital arrangements of electrons of the atoms of lithium, carbon, and

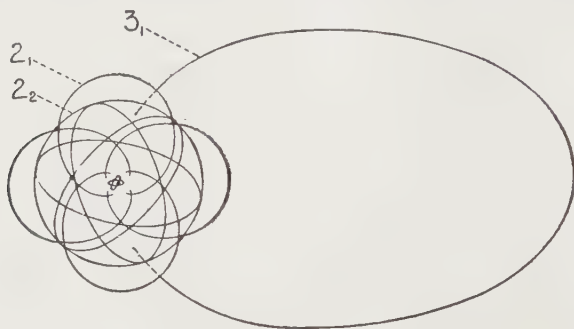


FIG. 43. Sodium (11).

sodium are shown in the accompanying diagrams (Figs. 41-43). The resemblance of lithium to sodium is evident; for the electron in the 2_1 orbit in lithium is similar to that in the 3_1 orbit of sodium. These electrons are the **valence electrons**, and they determine the characteristic chemical properties of the two metals.

88. **The Lewis-Langmuir Atom.** — Some years ago G. N. Lewis, an American chemist, propounded a theory according to which electrons either occupy fixed positions about the positive nucleus or vibrate about certain fixed positions. This theory has been developed by Irving Langmuir, another American chemist. It is often called the theory of the "cubical atom," the theory of the "static atom," or the "octet theory."

According to this theory, the electrons are either stationary or vibrate or oscillate about certain fixed positions so that the system of planetary electrons of any particular atom constitutes a symmetrical arrangement. It is assumed in case of the *lighter atoms* that the electrons arrange themselves in a series of concentric shells, the first containing 2 electrons, while all others tend to hold 8, these eight being placed symmetrically at the corners of a cube, or in pairs at the corners of a regular tetrahedron. No outer shell can contain more than 8 electrons, but the outer shell may contain a smaller number, depending upon the total number of electrons in the atom. The innermost shell would represent the nucleus. In the next or first shell there may be one or two electrons, one in the hydrogen atom and two in the helium

atom. In the case of helium, the arrangement would be particularly stable, for the electrons are assumed to be on diametrically opposite sides of the nucleus. With the exception of the hydrogen system, all atomic structures are assumed to have two electrons in the first shell.

The next outer shell is twice as far from the nucleus, and therefore has four times the superficial area, and may contain as many as 8 electrons. To illustrate, Li has one electron in this shell (Fig. 44). Li is represented as having an excess of 3 positive charges (protons) in the nucleus, *i.e.*, an atomic number of 3.

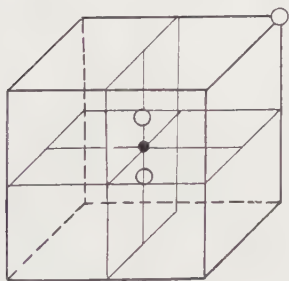


FIG. 44. Li.

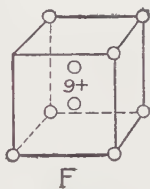


FIG. 45.

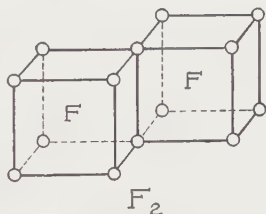


FIG. 46.

There is one electron in the second shell, and we may imagine that it is placed at one corner of a cube. Li has a positive valence of one.

In a similar way, we may represent *F* (at. no. 9). This is shown in Fig. 45. The atomic system of fluorine has 7 electrons in the second shell. *F* has, therefore, a negative valence of 1 or a positive valence of 7. A molecule of fluorine, F_2 , is represented in

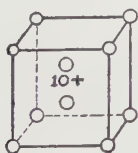
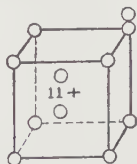
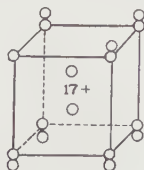
Ne
FIG. 47.Na
FIG. 48.Cl.
FIG. 49.

Fig. 46. Here the 2 atoms are pictured as sharing 2 electrons, giving a relatively stable system.

Ne (at. no. 10), like He, is an exceedingly stable system (Fig. 47). The arrangement of electrons is symmetrical and there are 8 of them in the second shell. The valence of Ne is zero.

Na (at. no. 11) is represented in Fig. 48. In this case, the external electrons are 11, so a new outer (third) shell is required. We may imagine this shell as being practically coincident with the second, and the first electron situated in the third shell occupies a position similar to that of the outside electron in the lithium atom. Na and Li have therefore similar properties, just as have He and Ne.

The chlorine atom (at. no. 17) is represented in Fig. 49. Cl has 7 electrons in the outside shell, and is therefore similar to F, both being univalent (negative) and ready to take on an electron to complete the circle of 8. This is shown clearly in the next

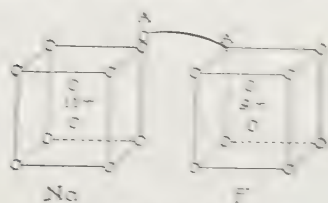


FIG. 50

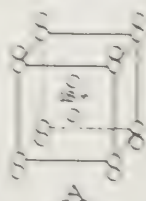
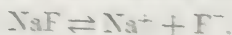


FIG. 51

diagram (Fig. 50), in which an atom of sodium is represented as giving up an electron to an atom of fluorine to form NaF. When NaF is dissolved in water, dissociation occurs



Such compounds as NaF, NaCl, etc., are called polar compounds, for they are potentially ionized; they contain polar or ionizable linkages between the oppositely charged ions (129).

When the sodium atom (Na) loses an electron, it becomes an ion (Na^+). It is seen, then, that certain atoms tend to borrow electrons in order to become stable systems. In certain molecular systems, however, borrowing and theft do not occur (see F_2).

Argon (at. no. 18) is similar to neon, except that there is a second layer of 8 electrons (Fig. 51).

With increasing atomic weights and atomic numbers, the systems become more complex, and it is assumed that the third shell may hold a maximum number of 18 electrons, while the fourth shell may hold as many as 32. The arrangement of electrons in the successive shells of the potassium atom (at. no. 19) is 2, 8, 8, 1. Since there is one electron in the outer shell, the valence of potassium is 1. What must be the electron arrangement for calcium (at. no. 20)?

The chemical properties of an element depend largely upon the number and arrangement of electrons in the outside shell, and the character of the chemical family to which it belongs. For most elements there is the same arrangement of electrons in the outside shell.

The names of the periodic families and groups are not in exact accord with those suggested by the chemical laws and principles to just outlined. However, such is a strange coincidence that the names were used — Valence and the strength of Valence and Molecular — pp. 12-13. When groups numbers were assigned as well as chemical families the grouping or classification of elements is still under discussion.

10. The Electron Theory of Valence. — The law of chemical union suggests very satisfactorily the number in case of the elements having inner electron groups. Thus, the elements of the alkali metals have a positive valence of one, for their atoms have one electron in the outside layer; the members of the alkaline earth family have a positive valence of two, for their atoms have two electrons in the outside layer; the elements of the alkaline earth family have a positive valence of two, for their atoms have two electrons in the outside layer; the elements of the alkaline earth family have a positive valence of one, for their atoms have one electron in the outside layer. The positive valence of an element is determined by the number of electrons in the outside shell and the negative valence by the number of electrons in the outside shell.

There will be the elements of the alkaline earth family which have two electrons in the outside shell, and a kernel of the nucleus and the inner shell is stable and a nucleus shell. In the case of some, two, and other more than two, it is concluded that there is a positive shell and that the whole atom is the kernel.

There have been some ideas that the periodicity of the groups of elements. The expression the number of electrons by the ordinary method, and the periodicity elements by date. Thus, a hydrogen atom would be represented by the symbol H, a lithium atom by Li, and an oxygen atom by O. The elements are hydrogen and oxygen are combining to form a chemical molecule, and then forming the nucleus of the atom which constitutes the kernel. The periodicity of a molecule of ordinary hydrogen is written H₂.

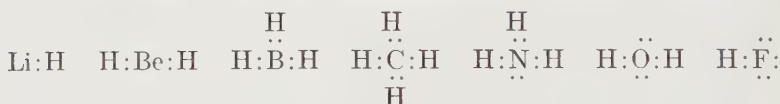
Atomic Weight of Valence. — Every element has both a positive and negative maximum valence, the sum of which is always equal and the positive valence corresponds to the group number. The atomic weight of the positive is the atomic group number to be as follows:

Group.....	0	1	2	3	4	5	6	7
Valence.....	0	+1	+2	+3	+4	+5	+6	+7
					-4	-3	-2	-1

The atoms may be grouped according to the number of outer (*valence*) electrons:



The number of outer electrons of an atom corresponds to the positive valence; thus, beryllium has a positive valence of 2, carbon a valence of 4, and fluorine a negative valence of 1 and a positive valence of 7. The *electronic formulae* of the hydrogen compounds of the elements in the first period may be written as follows:



The atoms of inert elements such as neon and argon are represented as having 8 electrons in the outer shell and, therefore, a valence of 0:



The hydrogen atom tends to surrender its electron to an atom of a more negative element, thus acquiring a valence of +1 (H^+). The tendency to rob hydrogen atoms of electrons is very strong in case of the very negative elements such as fluorine and chlorine. On the other hand, the elements which are more positive than hydrogen (e.g., K, Na, and Ca) tend to surrender electrons to hydrogen, giving it a valence of -1, as in KH and CaH_2 . The hydrogen atom in acquiring another electron resembles the halogen family, the atom of a member of which needs one electron to complete a structure similar to that of an inert or noble gas.

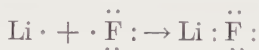
According to the electron theory of valence, an atom is "saturated" when it has 8 electrons in the outer sheath or shell regardless of the number of atoms to which it is linked, while under the old valence rule the emphasis is upon the number of atoms linked to the central atom.

The mutual attractions between the nucleus of one atom and the electrons of another are sufficient to account for the energy of formation of molecules, if a suitable arrangement of the electrons around the nucleus is assumed.

Among the numerical rules formulated by Lewis, are the following:

The Rule of Two: *The electrons tend to arrange themselves in pairs, as in Li : H.* There is usually an even number of electrons in the nucleus.

The Rule of Eight: *Every atom in a chemical compound tends to take on a configuration of its valence electrons similar to that of the nearest inert gas.* This is 2 for helium and 8 for neon, argon, etc. To illustrate, when fluorine combines with lithium to form lithium fluoride, we may represent the change thus:



When the fluorine atom takes on one more electron, it has a configuration similar to that of neon, the nearest inert gas:



It is interesting to note that paramagnetism is associated with the occurrence of an odd number of electrons in the molecule. Since oxygen is magnetic, the following electronic formula is assumed:



The union of calcium with oxygen may be represented thus:



There is a fuller discussion of valence in subsequent chapters (Chaps. VII, XV, and XXII).

90. **Isotopes.** — The atoms which compose the molecules of a pure elementary substance, such as oxygen (O_2), are alike; also, the same element may exist in different allotropic forms: *e.g.*, O_2 and O_3 (ozone). The differences in the properties of these substances are due to differences in internal structure and to their energy content.

There are cases in which a certain material exhibits nearly all the physical and chemical properties that are characteristic of an element and yet contains more than one kind of atom. The atomic weight and density of lead obtained from radioactive materials are appreciably different from those of ordinary lead, while the spectra of the various forms of the metal are almost

identical, and their chemical deportment appears to be identical. Two or more substances having the same atomic number and different atomic masses but occupying the same place in the periodic table of the chemical elements, are termed isotopes (68).

It has been shown that a number of the elements, such as neon, lithium, chlorine, and mercury, are isotopic mixtures. Aston has shown that neon is composed of 90 per cent of atoms of atomic weight 20.00, and about 10 per cent of atoms of atomic weight 22.00. Chlorine consists of atoms having atomic weights of 35 and 37, so mixed as to give the atomic weight 35.46.

PARTIAL TABLE OF ELEMENTS AND ISOTOPES (Aston)

Element	Atomic Number	Chemical Atomic Weight	Minimum Number of Isotopes	Atomic Weight of Isotopes in Order of Intensity
Li	3	6.94	2	7, 6
B	5	10.82	2	11, 10
Ne	10	20.2	3	20, 22, 21
Mg	12	24.32	3	24, 25, 26
Si	14	28.06	2	28, 29, (30)
Cl	17	35.46	2	35, 37
A	18	39.94	2	40, 36
Br	35	79.92	2	79, 81
Kr	36	82.91	6	84, 86, 82, 83, 80, 78
Hg	80	200.61	6	202, 200, 199, 198, 201, 204
S	16	32.06	3	32, 33, 34

No isotopes of H, He, F, P, Na, As, Al, and of some other elements are known. This indicates that these are pure elements, *i.e.*, only 1 atomic species can be recognized. Sn has 11 isotopes and Xe has 9.

According to F. W. Aston, an "element" should signify "a substance with definite chemical and spectrographic properties, which may or may not be a mixture of isotopes."

91. Positive-Ray Analysis. — Aston has developed a method for the measurement of atomic masses, termed positive-ray analysis. Positive rays, which consist of positively charged particles formed by the detachment of electrons from neutral atoms, were discovered by Goldstein in 1886. They are formed by electrical discharge through gases at low pressures. Under these conditions a gas undergoes ionization, *i.e.*, the neutral atom loses

an electron, forming a particle with a positive charge (Fig. 52). The simplest form of positive rays consists therefore of an atom of matter carrying a positive charge and moving in a direction opposite to that of the electron. The electron, the atomic unit of negative electricity, is always the same whatever its origin, but the positive ray depends upon the nature of the atom ionized.

By the Aston method, positive rays from a discharge tube are sorted out into a ribbon by employing two parallel slits, S_1 and S_2 (Fig. 52). The rays are then passed between positively and negatively charged plates P_1 and P_2 , as a result of which they are deflected toward plate P_2 , being spread out into an electric spectrum a portion of which passes through the diaphragm D .

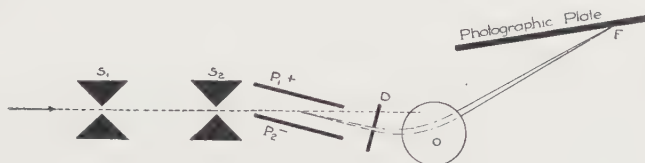


FIG. 52. Aston's Mass-Spectrograph.

By means of a powerful electromagnet, O , the spectrum is bent back so as to fall upon a photographic plate. All rays of a single charge and having the same mass converge at a focus F ; but rays having different masses will converge at different places. Mass spectra are therefore formed. Isotopes have different masses, so each one is characterized by a band on the plate. By an examination of the bands, it is possible to determine the masses of the different atoms (see Table).

92. Atoms Fundamentally the Same. — The discovery that certain elements having fractional atomic weights are mixtures of simple substances possessing atomic weights expressible in whole numbers, indicates that Prout's hypothesis may have a real foundation. The hydrogen nucleus (H^+) appears to be one of the two fundamental units which have to do with the building up of more complex nuclei or atoms, the other unit being the light negative electron. Since the helium nucleus has a mass of 4, it may be regarded as consisting of 4 hydrogen nuclei and 2 electrons closely packed together. The helium atom contains, in addition, 2 exterior electrons. But if the helium atom contains 4 hydrogen nuclei, why is not its mass 4.032, when that of the hydrogen atom is 1.008 ($4 \times 1.008 = 4.032$)? There is a loss in mass of 0.032

in the assumed transformation. In answering this question we must know that at present there is no real distinction made between matter and energy: matter is potential energy; and energy is potential matter. Therefore, when 4 hydrogen atoms are assumed to come together to form an atom of helium, the excess of matter, namely, 0.032, should appear as energy. It has been computed that the transformation of 1 g. of hydrogen to helium would liberate energy equivalent to 166,000,000,000 calories! The conversion of hydrogen to helium would yield, therefore, immense quantities of energy, such as is found in the sun; and it may be that this change accounts, at least in part, for the tremendous heat of the sun. It is very interesting to know that both hydrogen and helium are conspicuous in the sun; indeed, helium was discovered in the sun many years before it was found in terrestrial matter.

It should be stated that the experiments of F. W. Aston show that the average mass of the hydrogen nucleus, or proton, is very nearly 1.000 when packed in the nuclei of other atoms, which compares with its value of 1.008 in the free state. The helium nucleus of mass 4 is probably a secondary unit of great importance in the building of atoms. It has been suggested by W. D. Harkins and by E. Rutherford that hydrogen and helium are the fundamental "bricks" out of which all other elements have been built. According to the modern view, matter is granular in structure and electrical in nature, and atoms of positive and negative electricity — protons and electrons — may be regarded as the primordial atoms which nature has employed in element-building. The mass of an atom is measured by the number of protons in the nucleus, and the atomic number by the net positive charge of the nucleus, or the number of outer electrons which neutralize it.

93. The New Alchemy. — Scientists in their investigations of the atom have been able to discover only two ultimate entities, says Millikan, — positive and negative electrons — which are alike in the magnitude of their charge, but the positive electron (proton) is more than 1,800 times heavier than the negative electron. It is believed that the 92 elements are determined by the difference between the number of positive and negative particles which have been packed into the nuclei of the atoms. If this be true, it should be possible, theoretically at least, to transmute these elements into one another by a simple change in the particles packed in the nuclei of the atoms. As seen before,

this change is going on in the case of radioactive substances; that is, heavier atoms are transmuted into lighter atoms.

Rutherford and Chadwick of Cambridge University have bombarded atoms of various elements with alpha rays (a stream of helium ions, He^{++} , spontaneously expelled from the nucleus of a radioactive element), and have succeeded in expelling hydrogen nuclei from a number of different atoms, such as those of nitrogen, sodium, aluminium, and phosphorus. This means that artificial transmutation has been accomplished in these cases, but only on an exceedingly small scale. Rutherford has shown that the lighter atoms are the less stable; and most of the light atoms which he has decomposed have odd atomic numbers.

It has been suggested that the nitrogen atom ($N = 14$) is composed of $3\text{He} + 2\text{H}$, and the carbon atom ($C = 12$) of $3\text{He} = 3\text{He}^{++} + 6\ominus$, or 3 charged helium nuclei with 6 surrounding electrons. The elements having atomic weights divisible by 4 may be composed entirely of charged helium nuclei with attending electrons.

It has been suggested, therefore, by Harkins and by Rutherford that hydrogen and helium are the fundamental "bricks" out of which all other elements have been built. The decrease of the mass of the hydrogen atom from 1.008 in the hydrogen atom itself to exactly 1 in the other atoms, is said to be due, as already explained, to the "packing effect." Since the helium nucleus has a mass of 4 ($O = 16$), it may be regarded as consisting of 4 hydrogen nuclei and 2 electrons in very close combination. We may conclude, therefore, with Aston, that "elements are aggregations of atoms of positive and negative electricity"; also, that Prout's hypothesis (78) apparently has a real foundation.

While disintegration of atoms has been accomplished in a very slight degree, there is thus far no accepted case of the building up of atoms from simpler atoms.

Recent attempts have been made to transmute certain of the metals into other metals. Miethe and Stammreich of Germany announced in 1924 that they had been able to change mercury into gold by passing a current of high voltage through a quartz-mercury vapor lamp containing pure mercury. Also, in May, 1925, the Japanese scientist, Nagaoka, reported that he had effected the transmutation of mercury into gold by passing an electric discharge between terminals of tungsten and pure mercury. The atomic number of mercury is 80, while that of gold is 79. Mercury is an isotopic element, one of its atoms having a mass very close to the atomic weight of gold. If, therefore, the atomic number of mercury could be reduced to 79, a form of gold should result. If a proton, or hydrogen nucleus, could be ejected from

the nucleus of a mercury atom, gold should be formed. It is also conceivable that gold might be formed by knocking or firing an electron into the nucleus of a mercury atom, thereby reducing its atomic number from 80 to 79.

All this work has received a great deal of hostile criticism. It is possible that the mercury employed was not perfectly pure, or it may be that it became contaminated with gold from an outside source. According to "Nature," Professor Haber of Germany relates that one of his young collaborators found traces of gold in a material he was analyzing, but no other experimenter could confirm the observation on other samples of the material. It is possible that the trace of gold detected by the young chemist came from his gold spectacles which he was in the habit of removing.

In January, 1926, A. Smits of Holland reported the transmutation of lead into mercury and thallium by means of a quartz-lead vapor lamp, but his results are not generally accepted.

94. Summary and Supplementary. — The following statements are generally accepted:

(1) All matter is made up of molecules, atoms, or ions, which are in motion.

(2) Molecules are made up of atoms or ions.

(3) Atoms are made up of electrons and positive electricity, and contain vast stores of energy; *e.g.*, radium.

(4) Ions are atoms or groups of atoms which are charged through gain or loss of electrons.

(5) We know the number of atoms in a given quantity of matter, *e.g.*, the gram-atomic weight. We also know the approximate size and the mass of any atom.

(6) We know the mass and charge of the electron.

(7) We know that the positive electricity and the principal mass of the atom are concentrated in a nucleus which is very small in comparison with the size of the atom.

(8) Also, that most of the important properties of the atom depend upon the number and the arrangement of the electrons outside the nucleus, *i.e.*, upon the so-called "planetary electrons." We know this number, but still guess at the arrangement.

(9) We know that the atom as a whole is electrically neutral; also, that certain atoms have a tendency to give up outer electrons (*e.g.*, potassium), while others can take on or hold extra electrons (*e.g.*, chlorine).

(10) We also know the number of molecules in a given mass of a substance; and by means of X-rays we have learned how the atoms or ions are arranged in certain substances, such as sodium chloride, magnesium oxide, the diamond, calcite, copper, and iron.

EXERCISES

1. Name some elements which are amphoteric in nature, and explain and illustrate.
2. What was the electrochemical theory of Berzelius?
3. Briefly outline Prout's hypothesis. Why was it discarded by chemists, and why has interest been revived in it?
4. Explain and illustrate (1) Döbereiner's triads and (2) Newlands' law of octaves.
5. Outline the Periodic System. When and by whom was it proposed? State the chief applications of the Periodic Law.
6. What is meant by the Atomic Numbers of the elements? What general relation exists between the atomic numbers of elements and their atomic weights?
7. Explain why, when the elements are arranged according to their atomic numbers, their properties are recurrent.
8. Outline the Rutherford atom; also the Bohr atom.
9. What theory did Lewis and Langmuir propound concerning atomic structure? How does this theory explain the valences of such elements as helium, neon, sodium, and chlorine?
10. Upon what does the mass of an atom primarily depend? its chemical properties?
11. Define and illustrate what is meant by isotopes. (Outline the Aston method of positive-ray analysis.
12. Sketch the history of the atom from the days of the Greeks until the present time.
13. What are some of the positive statements we can make concerning the atom and its structure?
14. Have we any experimental evidence to show that one element may be transmuted into another? What change would be necessary in order to transmute mercury into gold?
15. When an alpha particle is expelled from the atom of an element, the latter is shifted two groups to the left in the Periodic System. Explain.
16. The loss of a beta particle (electron) shifts the element one group to the right in the Periodic System. Explain.

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PART II

THE NON-METALS

CHAPTER VI

OXYGEN AND OZONE. CATALYSIS

Owing to the great abundance, wide occurrence, and chemical activity of oxygen, it is a suitable element with which to commence the systematic study of the elements and their more important compounds. Oxygen is an element of the highest importance; for it is closely related to life, heat, and light.

In the systematic study of oxygen and other elements the following plan has been found to be a good one: (1) **History**; (2) **Occurrence**; (3) **Preparation**; (4) **Physical Properties**; (5) **Chemical Properties or Conduct**; (6) **Uses**.

OXYGEN. O = 16.000

95. **History of Oxygen.** — Joseph Priestley, an English chemist and clergyman, is usually regarded as the discoverer of oxygen. He prepared it, August 1, 1774, by heating mercuric oxide ("red precipitate") confined over mercury in an elongated glass vessel, the heat being obtained by the concentration of the sun's rays by means of a lens (Fig. 53). Priestley thrust a lighted candle into the gas and observed that it burned more brilliantly than in air, and for reasons that will be mentioned subsequently he named the substance "dephlogisticated air."

K. W. Scheele, an impoverished Swedish apothecary, prepared oxygen in 1771-1772; but he did not publish the results of his researches until 1777. He heated various substances, such as manganese dioxide and saltpeter. Scheele's research upon the black oxide of manganese (MnO_2) was a brilliant piece of work. During this investigation he discovered chlorine, oxygen, manganese, and baryta (BaO). Despite his limited facilities for experimenting, Scheele was one of the greatest chemists of all time.

Lavoisier, a renowned French chemist who is sometimes called

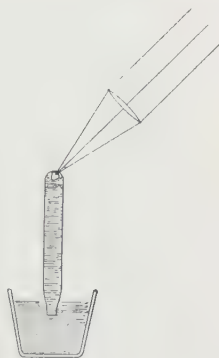


FIG 53.

"the father of modern chemistry," took up the study of the properties of oxygen, and in 1777 carried out his classical experiment to show the relation of the gas to air. By means of a charcoal fire he heated mercury confined in a retort, the neck of which passed up through a vessel containing mercury into a bell-jar with air in it (Fig. 54). The mer-

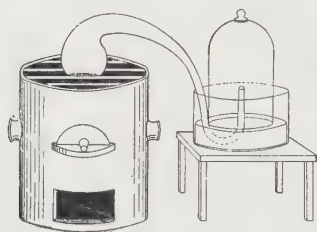


FIG. 54.

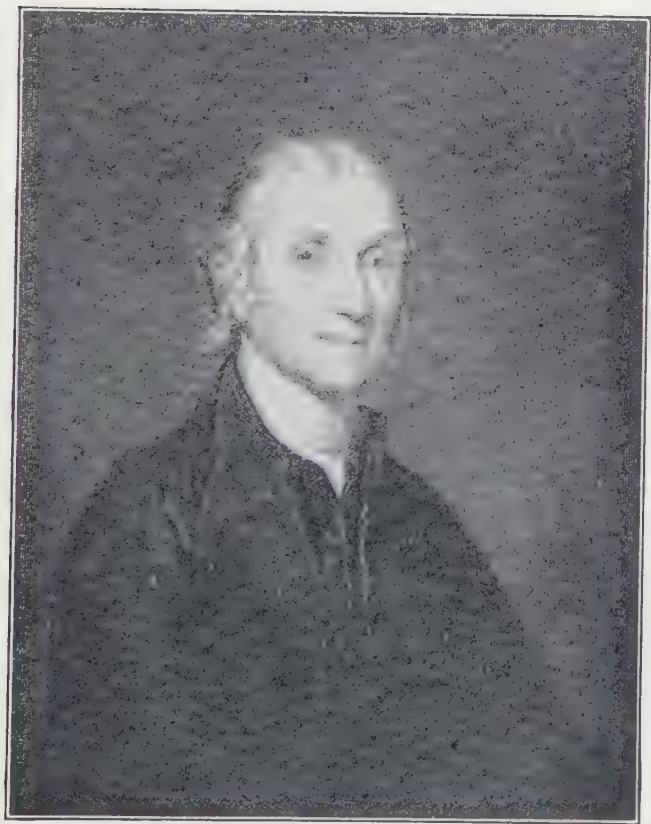
cury and air (50 cubic inches at 28 inches of mercury and 10°) were heated for 12 days, at the end of which he observed that the air had lost about one-fifth of its original volume (the volume was reduced from 50 to between 42 and 43 cubic inches). The red powder formed was removed from the retort and

heated in another vessel; it yielded a volume of an active gas equal to the decrease in the volume (7 to 8 cubic inches) of the original air. This gas was oxygen. The gas left in the retort would not combine with mercury, extinguished a burning candle, and a mouse was quickly suffocated in it. Lavoisier named it *azote* (nitrogen). The proof was now complete that oxygen is a component of the air. Subsequently, Lavoisier named the active gas **oxygen** (Greek, "*acid-producer*"), for he thought it was an essential constituent of all acids. The word is a misnomer, however, for there are acids, *e.g.*, hydrochloric acid, that contain no oxygen.

96. Occurrence. — Oxygen occurs abundantly as a colorless gas having the molecular formula O_2 . In the free state it makes up about one-fifth of the air by volume and nearly one-fourth by weight. Oxygen in combination constitutes nearly 50 per cent of terrestrial matter, and also a very large part of such common substances as limestone, brick, and mortar. Oxygen also occurs in the sun, stars, and nebulae. It is an essential constituent of animal and vegetable matter. Indeed, it is the most abundant element known.

97. Preparation. — Oxygen is usually prepared on a small scale by heating substances containing it, such as oxides and chlorates; it is also prepared by the interaction of sodium peroxide and water. On a commercial scale, oxygen is obtained largely from liquefied air and by the electrolysis of water.

I. Preparation of Oxygen by Heating Oxides and Salts Rich in Oxygen.



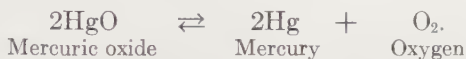
JOSEPH PRIESTLEY (1733-1804)



ANTOINE LAURENT LAVOISIER (1743-1794)

(1) *By heating the oxides of the more inactive metals, such as those of mercury, silver, gold, and those of the platinum metals.*

Priestley obtained it by heating mercuric oxide:



The oxide may be heated in a test-tube with a delivery tube leading to a pneumatic trough, and the gas is collected by the downward displacement of water, as shown in Fig. 55. This method is of historical interest, but is too expensive. The action is reversible, for HgO can be formed by heating mercury in air (95).

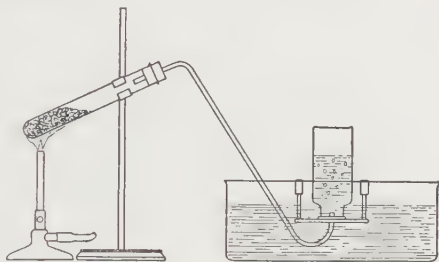


FIG. 55.

(2) *By heating higher oxides.*

Oxygen cannot be prepared by heating the lower oxides of metals other than those mentioned above, but it may be obtained by heating certain higher oxides including peroxides. Barium peroxide, hydrogen peroxide, and manganese dioxide will illustrate this method:



Brin's process for the manufacture of oxygen is based on this reaction. When BaO is heated in air to about 500° , it combines with oxygen to form the peroxide BaO₂. When BaO₂ is heated to about $1,000^\circ$, it loses one unit of oxygen, forming BaO. By regulating the gaseous pressure it has been found that this operation can best be carried out at about 700° . Air is first forced into the tubes containing BaO, nitrogen being allowed to escape through a valve at the other end of the tube. When the formation of BaO₂ is complete, the pumps are reversed and at the reduced pressure BaO₂ loses oxygen to form BaO. The advantage of the Brin process lies in the fact that a limited amount of the lower oxide of barium can be used repeatedly.

Hydrogen peroxide (H₂O₂) readily loses oxygen to form water:



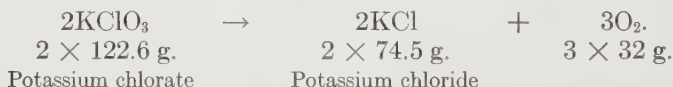
Manganese dioxide occurs abundantly in nature as the mineral *pyrolusite*. At a high temperature it decomposes thus:



(3) *By heating certain salts rich in oxygen.*

Oxygen is evolved when certain salts rich in oxygen are heated. For example: chlorates, bromates, nitrates, or permanganates.

Potassium chlorate (KClO_3) is the most convenient source of oxygen for the common laboratory experiments. The gas can be liberated by heating a small quantity of potassium chlorate in a hard glass test-tube. The white crystals of the salt melt at 357° , and at 380° bubbles of oxygen are evolved. A glowing splinter thrust into the tube burns brilliantly. The chemical change is shown by the following equation:



This equation shows that 96 g. of oxygen may be obtained by heating 245 g. (2 gram-molecular weights) of potassium chlorate.

The production of oxygen is greatly accelerated by mixing the potassium chlorate with manganese dioxide (MnO_2). The manganese dioxide undergoes no permanent change, and it may be recovered at the end of the action by dissolving the potassium chloride in water. The mere presence, then, of manganese dioxide increases the speed of the reaction, and the generation of oxygen is accomplished at a much lower temperature — below 200° .

The gas may be readily prepared for laboratory use by heating 5–10 g. of potassium chlorate with about one-fourth of its weight of manganese dioxide, as shown in Fig. 55.

Warning. — *Manganese dioxide is sometimes adulterated with organic matter, which may cause a violent explosion when heated with potassium chlorate! It may be tested before using by heating in a test-tube about half a gram of it mixed with an equal weight of the chlorate.*

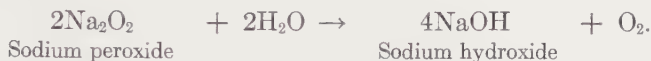
Oxygen may also be produced by heating sodium or potassium nitrate:



II. By the Interaction of Sodium Peroxide and Water.

Oxygen may be prepared very conveniently by treating sodium peroxide ("oxone") with water. Generators similar to those used for acetylene are well adapted for the purpose.

The preparation of oxygen can be easily shown by allowing water to fall from a dropping-funnel upon sodium peroxide (Na_2O_2) contained in a flask. A delivery tube runs from the flask to the trough.



III. Commercial Preparation of Oxygen.

A number of methods have been employed for the manufacture of oxygen (see Brin's process); but in the United States, at the present time, nearly all the oxygen is obtained commercially as follows:

(1) *From Liquefied Air.*

The boiling point of liquid oxygen is -182.5° and that of nitrogen -194° ; therefore, when liquid air evaporates, the more volatile nitrogen escapes first, and the residual oxygen is finally pumped into strong steel cylinders and thus stored for commercial use. The gas thus prepared usually contains from 95 to 98 per cent of oxygen. This method of preparing oxygen is purely physical. It is the chief commercial process.

(2) *By the Electrolysis of Water.*

When some sodium hydroxide is added to water contained in an iron tank and a current of electricity passed through the solution, very pure oxygen is liberated at the anode and hydrogen at the cathode. This method yields gas of high quality, but is more expensive than the former one. Water is usually decomposed by the current to obtain the hydrogen, oxygen being obtained as a by-product.

98. Physical Properties of Oxygen. — In general, six specific physical properties will be mentioned in describing a gas: (1) *color*, (2) *odor*, (3) *taste*, (4) *density*, (5) *conditions for liquefaction*, (6) *solubility* — in water unless another solvent is specified.

Oxygen has the following properties:

(1) It is a colorless, odorless, tasteless gas.

(2) The weight of one liter of the gas at 0° and 760 mm. (1 atmosphere) pressure is 1.42900 g. (Morley). This weight is often used as the density of oxygen; but, strictly speaking, the

density of a substance is the weight of 1 cubic centimeter (cc.); hence the density of oxygen is 0.001429, *i.e.*, $1.429 \div 1000$.

(3) The specific gravity (relative density) of oxygen (air = 1) is 1.105. The sp. gr. of a gas may be found by dividing the weight of a liter of the gas by the weight of a liter of the standard gas. As a liter of air weighs 1.293 g. under the same conditions that a liter of oxygen weighs 1.429 g., the sp. gr. of oxygen referred to air

$$\text{is } \frac{1.429}{1.293} = 1.105.$$

The sp. gr. of oxygen referred to hydrogen is

$$\frac{1.429}{0.08987} = 15.9.$$

(4) Oxygen can be liquefied at -118.8° and under a pressure of 49.7 atmospheres. -118.8° is known as the **critical temperature** (C.T.) of oxygen. It is impossible to liquefy oxygen above its critical temperature, no matter how great may be the pressure applied. The pressure required to liquefy a gas at its C.T. is called the **critical pressure** (C.P.). Oxygen, therefore, has a C.P. of approximately 50 atmospheres. The density of liquid oxygen is 1.13, *i.e.*, 1 cc. of it weighs 1.13 g. Liquid oxygen has a pale-blue color, and is strongly magnetic. It boils at -182.5° in an open vessel (1 atmosphere pressure). Dewar froze oxygen to a pale-blue solid by cooling liquid oxygen with liquid hydrogen. The snow-like solid melts at -219° .

(5) Oxygen is slightly soluble in water; 100 cc. of water dissolve, at 0° , 4.89 cc. and at 20° , 3.1 cc. of the gas, measured under 760 mm. of pressure. Fish are dependent upon the oxygen dissolved in water. The solubility of oxygen in sea-water is about 78 per cent of that in pure water.

99. Chemical Properties of Oxygen.—In the study of the chemical properties of a substance, we consider its ability to interact with other substances, the conditions under which the chemical actions occur, the speed of the actions, the properties and composition of the products formed, and the energy changes accompanying the chemical changes.

Oxygen is a very active element, particularly at high temperatures, for it enters into vigorous combination with many different substances. It has chemical properties similar to those of the air, but it is much more active, being a powerful supporter of combustion.

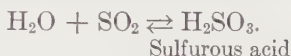
I. Oxygen and the Non-metals.

Oxygen enters into direct combination with all the non-metals, excepting the halogens and the inactive gases of the atmosphere.

(1) When burning sulfur contained in a deflagrating spoon is thrust into oxygen, it burns more vigorously, forming sulfur dioxide, a colorless gas with a sharp odor:



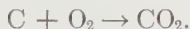
Sulfur dioxide dissolves freely in water, forming sulfurous acid:



The solution has a sour taste and turns blue litmus red, which is a characteristic of a class of compounds called acids. Sulfur dioxide is termed an **acidic oxide** or **anhydride**; for it interacts with water to form an acid. When a molecule of unstable sulfurous acid breaks down, it forms a molecule of water and a molecule of its anhydride (Greek, meaning *without water*).

Fundamental fact: Oxides of certain non-metallic elements (anhydrides) interact with water to form acids, which turn blue litmus red.

(2) When finely divided charcoal (carbon) is heated in an iron pan and poured into a jar of oxygen (Care!), it burns brilliantly, forming carbon dioxide:

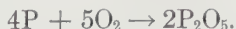


Carbon dioxide, like sulfur dioxide, dissolves in water, forming a weak, unstable acid:

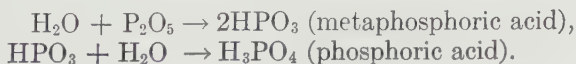


Carbon dioxide is therefore the anhydride of carbonic acid.

(3) When a very small piece of white phosphorus is heated carefully in a deflagrating spoon and then plunged into a jar of oxygen, it burns with the production of intense heat and light, forming phosphorus pentoxide (P_2O_5):



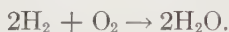
Phosphorus pentoxide forms a white smoke, which gradually dissolves in water, forming phosphoric acid:



In cold water metaphosphoric acid is first formed, which gradually combines with more water to form ordinary phosphoric acid.

Warning. — *Great care must be exercised in handling white phosphorus!*

(4) A jet of hydrogen burns in an atmosphere of oxygen, forming water:

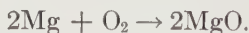


It is also true that a jet of oxygen will burn in an atmosphere of hydrogen to form water. These facts show that combustion is a relative matter, or that the terms combustible and supporter of combustion are purely relative.

II. Oxygen and the Metals.

All familiar metals, excepting the noble metals, silver, gold and the platinum metals, when heated, unite with oxygen.

(1) The alkali and the alkaline earth metals (76) are the most active of the metals, and they unite readily with oxygen, forming **basic oxides**. When a magnesium ribbon is heated in the flame of a burner, and then thrust into a vessel containing oxygen, it burns with dazzling brilliancy, forming magnesium oxide, or magnesia, MgO :



Magnesium oxide is a white powder and is sparingly soluble in water. When thoroughly treated with water, it forms a very dilute solution of magnesium hydroxide, a base:



Water solutions of bases have a soapy taste and the general characteristic of turning red litmus blue. Acids and bases are very different in their chemical conduct.

Fundamental fact: Oxides of the more active metals interact with water, forming bases; therefore they are called **basic oxides**.

Some other very important oxides and bases are the following:

<i>Oxide of Metal</i>	<i>Water</i>	<i>Base</i>
Na_2O	+ $\text{H}_2\text{O} \rightarrow 2\text{NaOH}$,	Sodium hydroxide
K_2O	+ $\text{H}_2\text{O} \rightarrow 2\text{KOH}$,	Potassium hydroxide
CaO (lime)	+ $\text{H}_2\text{O} \rightleftharpoons \text{Ca}(\text{OH})_2$,	Calcium hydroxide

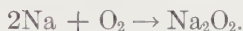
(2) Iron will burn in an atmosphere of oxygen. This may be shown by coating the end of a bundle of fine iron wire with sulfur, igniting the latter, and then thrusting the bundle into a jar of

oxygen. The metal burns with brilliancy, forming *magnetic oxide of iron*:



Magnetic oxide of iron is identical with hammer-scale; it is a black, brittle substance and entirely different from *iron rust* (ferric oxide, Fe_2O_3). The oxides of iron are insoluble in water, as are most oxides of heavy metals. They do not therefore interact with water to form alkalies or bases.

(3) Sodium burns in oxygen to form sodium peroxide:



100. Tests for Oxygen. — (1) Oxygen is a colorless, odorless, tasteless gas, and causes a glowing splinter of wood to burst into flame. The only other gas which kindles into flame a glowing splinter is nitrous oxide ("laughing gas").

(2) Oxygen unites readily with nitric oxide (NO), forming red-brown fumes (NO_2), while nitrous oxide (N_2O) has no action with nitric oxide.

101. Combustion. — Combustion, in the popular sense, is the rapid chemical union of matter with oxygen, accompanied by the evolution of heat and light. Fire consists of heat and light produced by the rapid union of fuel with oxygen.

The relation of oxygen to combustion can be shown by floating a burning candle upon water and inverting a cylinder over it as shown in Fig. 56. In a short while the

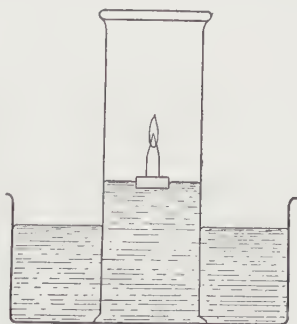


FIG. 56.

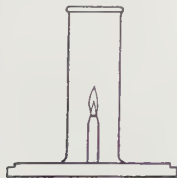


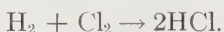
FIG. 57.

light grows dim and the candle goes out. When the oxygen in the air is reduced below a certain percentage, it will no longer support combustion.

When fuel burns, the chief products of combustion (in certain cases the only ones) are water and carbon dioxide. This can be demonstrated by inverting a dry cylinder over a burning candle (Fig. 57). In the course of a few minutes water appears on the inside of the jar. By in-

verting the jar and adding some limewater (a solution of calcium hydroxide) and then shaking, a white precipitate of calcium carbonate is obtained. This is a test for carbon dioxide.

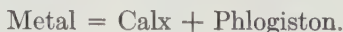
Combustion, in the scientific sense, is any act of chemical combination accompanied by the evolution of heat and more or less light. In other words, combustion can take place in which oxygen plays no part: *e.g.*, chlorine gas will burn in an atmosphere of hydrogen, forming hydrochloric acid gas (HCl):



Both heat and light are produced, and this is as truly combustion as is the rapid union of hydrogen and oxygen to form water.

The correct explanation of combustion was made by Lavoisier soon after the discovery of oxygen by Priestley in 1774. Before his day, all theories of combustion were erroneous. The most fascinating of these was the Theory of Phlogiston which will be discussed in the next section.

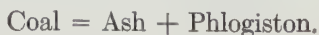
102. Theory of Phlogiston. — An interesting theory of combustion, known as the Theory of Phlogiston, held sway during the latter part of the seventeenth century and most of the eighteenth. J. J. Becher (1635–1682), a German chemist, held that certain substances contained an inflammable material (*terra pinguis*, Latin, meaning *fatty* or *inflammable earth*). George Ernst Stahl (1660–1734), professor at Halle, was a good chemist and a successful teacher; he popularized and extended Becher's views and gave the name **phlogiston** (Greek, *burnt, combustible*) to his *terra pinguis*. According to Stahl, when bodies burned or were calcined, phlogiston escaped from them with a whirling motion. Very combustible bodies were supposed to be rich in phlogiston. When a metal was calcined, phlogiston escaped and a **calx** was formed. Stahl's idea of calcination may be expressed thus:



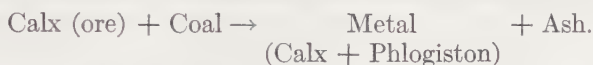
Our modern statement is:



According to the phlogiston theory, a combustible substance, such as coal, was supposed to be very rich in phlogiston, and on being burnt it left very little ash:



When metallic oxides, or ores, were reduced by heating with coal or charcoal, it was regarded as a transfer of phlogiston from the coal to the calx or ore, a metal and an ash being formed:



The withdrawal or escape of phlogiston is equivalent to oxidation, and the addition of phlogiston is the equivalent of reduction. It was known to the phlogistians that the product obtained by calcining or burning a metal weighed more than the substance which was burned, but it was argued that phlogiston was so light that it buoyed the body up; consequently, when it lost phlogiston, it weighed more!

The doctrine of phlogiston was firmly advocated by the leading chemists of the eighteenth century, such as Priestley, Cavendish, and Scheele. The theory was finally overthrown by Lavoisier who published his oxidation theory in 1777.

The overthrow of the phlogistic theory was one of the greatest achievements of Lavoisier.

103. Kindling Temperature. — The kindling temperature or ignition point of a substance is the temperature to which the substance must be heated in order to start combustion. Kindling temperatures of different substances vary within wide limits. Thus, white phosphorus ignites at 35°, carbon disulfide at about 150°, and ordinary gases at much higher temperatures. The ignition point of a substance is not very definite, for it depends upon certain variables, such as the fineness of material, pressure, and catalytic agents.

The ignition temperature should not be confused with the temperature of reaction: *e.g.*, phosphorus has a very low ignition temperature, but its temperature of reaction is very high.

In this connection it is of interest to note that the ignition temperature of methane or marsh gas (CH₄) is in the neighborhood of 700°. A temperature of about 1,350° may be obtained by heating an ordinary laboratory furnace by a gas-wind flame. The approximate temperatures of the glowing interior of the furnace are as follows:

Incipient red heat.....	550°
Dull red heat.....	650°
Red heat.....	800°
Bright red heat.....	1,000°
Yellow heat.....	1,200°
White heat.....	1,350°

104. **Spontaneous Combustion.** — Certain substances, *e.g.*, phosphorus, zinc ethyl, and the hydrides of silicon, catch fire spontaneously when exposed to the air; they all have very low kindling temperatures. Why do coal, hay-stacks, and greasy or oily rags sometimes ignite spontaneously? To understand this question, it is of fundamental importance to know that the amount of energy given out when a definite amount of a substance, *e.g.*, carbon, combines with oxygen is the same whether the change takes place rapidly or slowly. In case the combination of the material with oxygen proceeds slowly and the material is so exposed to the air that the heat is rapidly dissipated, the temperature does not rise to the ignition point; but if the material is so exposed to the air that the heat accumulates, the temperature may rise until the ignition point is reached. Now such materials as piles of rags are poor conductors; furthermore, certain oils and fats have a tendency to absorb and combine with oxygen, producing heat. If combination with oxygen proceeds until the kindling temperature is reached, the material bursts into flame.

Certain solid substances when very finely divided may ignite spontaneously. Thus, lead prepared by the ignition of lead tartrate ($\text{PbC}_4\text{H}_4\text{O}_6$) will glow brightly when exposed to the air, yellow fumes of lead oxide (PbO) being formed. This form of the metal is termed *pyrophoric lead*.

Many disastrous fires have been started by spontaneous combustion.

Natural fires have originated in various ways. For instance, in connection with volcanoes, earthquakes, lightning, meteorites, or friction. During the earthquake at Bavispe, Mexico, in May, 1887, fires originated from the friction of falling stones. A globule of dew or balsam has started fire by focusing the sun's rays upon very combustible material. Wood¹ may be scorched, or possibly set on fire, by employing a flask of water as a lens for concentrating the rays of the sun.

105. **Explosions.** — It is well known that when certain gases or very finely divided substances are mixed with the proper pro-

¹ More than a quarter of a century ago the writer was delivering a lecture on chemistry at Richmond, Kentucky, when his attention was attracted by smoke a few yards away. There was a flask of water standing on a wooden table in front of a window through which the sun was shining brightly, and the conditions happened to be so favorable for concentrating the sun's rays, that the table was scorched.

portions of air or of oxygen, they will explode if the mixture be ignited by a spark, match, or otherwise.

An explosion is due to very rapid combustion of certain gaseous mixtures, such as illuminating gas and air, or to finely divided organic matter — charcoal, coal, flour, starch, etc. — suspended in air. The ignition of the mixture usually starts at one point, and the speed of explosive combustion increases rapidly until a maximum speed is attained.

Some terrific explosions have occurred in flour mills and other factories, so today the modern mills are equipped with elaborate dust removing installations, and machinery likely to develop sparks of electricity by friction is grounded.

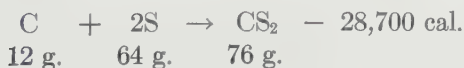
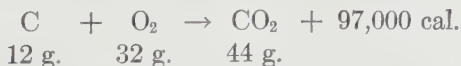
It is well known that there are explosions of other types: *e.g.*, the rapid decomposition of such substances as nitroglycerine and T.N.T. (trinitrotoluene).

106. Heat of Combustion. — The heat given out when substances burn is called heat of combustion. Heat is expressed in calories. A **calorie** is the amount of heat required to raise 1 g. of water 1° C. (from 15°–16°). This unit is the *gram-calorie*. The abbreviation is *cal*. Sometimes a unit 1,000 times as great is used (Cal.). This is the *kilogram-calorie*. Heat of combustion is measured in an apparatus known as a **calorimeter** (Greek, *heat-measurer*). A given mass of the body is burned in an inner vessel in such a way that the heat developed is imparted to a known mass of water. By noting the rise in the temperature of the water, the amount of heat given out can be readily calculated. (See Thermochemistry.)

Engineers very commonly use the **British Thermal Unit** (B.T.U.). This is the amount of heat required to raise 1 pound of water 1° F.

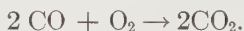
1 B.T.U. = 252 calories, for 1 pound is equal to 453.6 g., and 1° F. to 5/9° C.; therefore, $453.6 \times 5/9 = 252$.

Chemical changes accompanied by the evolution of heat are called **exothermic**. Those in which heat is absorbed as the action continues are known as **endothermic**. Thus, the combustion of carbon and oxygen is exothermic, while the interaction of sulfur and carbon to form carbon disulfide is endothermic:



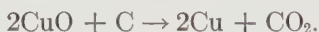
As a rule, exothermic substances are more stable than endothermic substances. Thus, water, carbon dioxide, magnesia (MgO), and lime (CaO) are all formed by the evolution of much heat, *i.e.*, they have a high heat of formation, and their stability is well known. On the other hand, ozone, carbon disulfide, and acetylene are endothermic substances, *i.e.*, they have a negative heat of formation, and are consequently unstable. The heat of formation of compounds may therefore give some indication of their relative stability.

107. Oxidation. — The combination of a substance with oxygen is known as oxidation. The products of oxidation are called **oxides**. Thus, carbon monoxide will burn when heated in air or oxygen, forming carbon dioxide:



Many very important compounds belong to this class: *e.g.*, hydrogen monoxide or water, H_2O ; hydrogen peroxide, H_2O_2 ; quicklime, CaO ; silicon dioxide (quartz, sand, gravel, etc.), SiO_2 ; sulfur dioxide, SO_2 ; Fe_2O_3 , ferric oxide.

Reduction is the converse of oxidation: *e.g.*, when copper oxide is mixed with finely divided charcoal and the mixture heated, the carbon (charcoal) robs the compound of its oxygen, forming CO_2 :



The term oxidation is a broad one, for it includes the combustion of substances in air or oxygen, the rusting of metals, decay of animal and vegetable matter, and the change which occurs in animals during respiration.

We have already seen that oxidation may be either slow or rapid, and that the same amount of heat is liberated in the two cases, provided that the same kinds and quantities of substances undergo oxidation.

Various attempts were made by the early chemists to explain the rusting of metals. It was known that the rusts (oxides) were heavier than the metals and it was supposed that something was taken from the air; but it was Lomonossov (1756) who first proved experimentally that the extra substance did come from the air (95).

The rusting of iron may be shown by sprinkling iron filings over the inside of a wet test-tube, and then inverting it over water. In the course of time about one-fifth of the gas confined in the

tube disappears, and water rises to take its place. Not only does this experiment prove what rusting is, but it shows incidentally that about one-fifth of the air by volume is oxygen.

Oxygen plays an important rôle in change and decay, which is seen upon every hand. Carbon and hydrogen of vegetable matter are oxidized to water and carbon dioxide. We oxidize fuel in order to obtain energy to carry on most of the work of the world. The oxygen dissolved in water is very important in the disposal of sewage. The latter is mixed with large volumes of water, not simply to dilute the sewage but for the object of having it undergo oxidation by coming in contact with dissolved oxygen. Slow oxidation takes place in the bodies of animals. The oxygen of the inspired air combines with the *hemoglobin* in the red-blood corpuscles to form an unstable compound (*oxyhemoglobin*) which circulates throughout the body and oxidizes to water and carbon dioxide the carbon and hydrogen absorbed during digestion. During this oxidation process heat is given out, which is of the greatest importance in keeping the body warm.

108. Oxidizing Agents. — An oxidizing agent is a substance which gives up oxygen more or less readily to other substances. The following are a few of the very important oxidizing agents:

Sodium peroxide.....	Na_2O_2
Hydrogen peroxide.....	H_2O_2
Manganese dioxide.....	MnO_2
Potassium chlorate.....	KClO_3
Potassium nitrate.....	KNO_3
Potassium permanganate.....	KMnO_4
Sodium hypochlorite.....	NaClO
Nitric acid.....	HNO_3

The activity of potassium permanganate may be shown by stirring some of the finely divided substance into two or three cc. of glycerine; the latter ignites.

We have already seen that some of these compounds part with oxygen rather readily, and are therefore used in the preparation of that gas. Moist sodium peroxide sometimes sets fire to paper; potassium nitrate is a component of ordinary gunpowder, so when a gun is fired the niter furnishes the oxygen which takes part in the combustion inside the gun; and it is known to all how readily hydrogen peroxide yields oxygen.

109. Uses of Oxygen. — Not only is oxygen the most abundant element, but it is the most useful; for life, heat and light are largely dependent upon it. Oxygen is of great value in the disposal of

sewage and in the oxidation of waste matter in general. Considerable quantities of oxygen are used for cutting and welding metals by the oxyacetylene, the oxyethylene, or the oxyhydrogen blowpipe; in aviation, submarines, and in caisson tunneling; in the oxidation of linseed oil; in medicine for treating cases of pneumonia, in gas-poisoning, and to mix with nitrous oxide ("laughing gas") when the latter is administered as an anaes-



Courtesy, U. S. Bureau of Mines.

FIG. 58. Gibbs Apparatus, developed by Bureau of Mines; supplies oxygen for two hours or more.

thetic; for enriching air in the blast furnace and the steel converter; and in mines (Fig. 58.)

The production of oxygen has greatly increased within the last fifteen years.

110. The Speed of Oxidation. — The speed of oxidation of materials or substances varies greatly. In some cases it is so slow as to escape detection by ordinary means; in other cases it is so rapid that it is pronounced combustion or even explosion. Speed of oxidation depends not only upon the nature of the substance, but upon conditions — temperature, concentration, fineness of material, and catalytic agents. The effect of temperature, concentration of oxygen, and fineness of material are well illustrated in the case of iron. An iron bar rusts slowly when exposed to air, which is about one-fifth oxygen by volume; but when a

bundle of iron wire is heated to a high temperature in contact with oxygen, the metal burns brilliantly. Finely divided iron may be burned by sprinkling it in the flame of a gas burner. When matter is finely divided, a large surface is exposed to air or oxygen, and the chances of the particles (molecules) of oxygen and iron coming in contact are greatly increased. Everyone knows the value of shavings in kindling a fire. Again, finely divided platinum (catalytic agent) will cause a mixture of oxygen and hydrogen to explode. Platinum is also very important in speeding up the union of SO_2 and oxygen in the production of SO_3 for the manufacture of sulfuric acid.

OZONE

111. **History.** — M. van Marum, a Dutch chemist, noticed in 1785 a peculiar odor when electric sparks had been passed through air or oxygen. He also observed that the substance formed was able to tarnish mercury. Schönbein (1840) showed that the substance with a characteristic odor was capable of oxidizing various substances. He named it **ozone** (Greek, meaning *smell*). Andrews (1856) established the elementary character of ozone.

112. **Occurrence.** — A very small quantity of ozone appears to be present in the atmosphere, particularly in the upper region, where the ultra-violet light rays have the greatest effect upon oxygen. Ozone formed in the upper dust-free atmosphere would find its way to the lower atmosphere, because of the circulation of the air. It is likely that small quantities of ozone are formed during thunderstorms, on account of the action of electricity (energy) upon oxygen. Any ozone thus formed would no doubt be destroyed rapidly by coming in contact with dust particles, etc., of the air. It is clear that there is some active oxidizing substance in the air, but it is likely that certain oxidizing effects attributed to ozone are induced by very small quantities of hydrogen peroxide or of oxides of nitrogen. Even under the most favorable conditions in country or sea air, the quantity of ozone is exceedingly small.

113. **Preparation.** — Ozone ("ozonized oxygen") is formed by subjecting oxygen to the action of electric waves. Many types of apparatus have been used, but one of the most convenient is Siemen's ozonizer as shown in Fig. 59. Two glass tubes are arranged coaxially, the smaller one being coated within and the larger one without with an electric conductor (silver or tin-foil).

Each coating is connected with a wire from an induction machine, and dry, cool oxygen, circulating in the space between the tubes, is subjected to the action of electric waves. As ordinarily conducted, this method yields a low percentage of ozone; but by cooling the oxygen to 0° , using a powerful coil and avoiding sparks, even as high as 25 per cent of oxygen may be transformed into the more active ozone. Ozonized oxygen contains, as a rule, 6 to

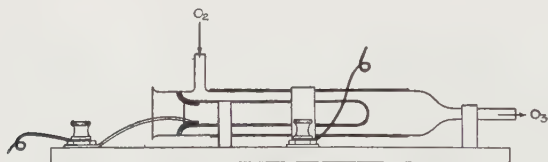


FIG. 59.

7 per cent by volume of ozone. To prepare pure liquid ozone, the mixture of oxygen and ozone is cooled with liquid air.

It is interesting to know that ozone may be formed in several other ways, such as, (1) by suspending a stick of freshly scraped phosphorus in a stoppered bottle containing some water; (2) ozone is evolved in small quantities at the anode by the electrolysis of water; (3) by the interaction of fluorine and water; (4) by the action of concentrated sulfuric acid on barium peroxide, potassium permanganate, etc.; (5) by the action of ultra-violet light on oxygen.

The following *experiments* may be performed to illustrate the powerful oxidizing action of potassium permanganate when mixed with concentrated sulfuric acid:

Place three 250 cc. beakers on a table and pour into each about 2 g. of pulverized potassium permanganate and then moisten it with a few drops of water.

(a) Pour about 2 cc. of concentrated sulfuric acid into the first beaker, and then pour in from a test-tube fastened to a stick 1 cc. of alcohol (Care! the alcohol ignites).

(b) Pour sulfuric acid into the second beaker, as before, and then ignite illuminating gas by allowing it to flow into the beaker through a glass tube.

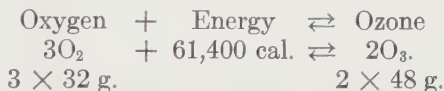
(c) After pouring sulfuric acid into the third beaker, stir its contents with a glass rod, then bring the rod in contact with the wick of an alcohol lamp.

114. Tests for Ozone. — (1) Ozone has a characteristic odor; (2) it turns potassium iodide — starch paper blue, on account of the liberation of iodine. In applying this test the chemist must remember that certain other substances, such as hydrogen peroxide,

chlorine, and certain oxides of nitrogen, also liberate iodine from potassium iodide.

115. Physical Properties. — Ozone is a blue gas possessing a sharp odor. If more than 1 part of ozone is present in 20,000 parts of air it irritates the mucous membrane when breathed, and is poisonous. Ozone may be condensed to an indigo-blue liquid, which boils at -112° . When ozonized oxygen is therefore passed into a tube surrounded by liquid oxygen, the ozone is liquefied. The weight of a liter of ozone gas is 2.140 g., so its specific gravity is 1.5 times that of oxygen, both gases being measured at 0° and 760 mm. (S.T.P.). Ozone is much more soluble in water than is oxygen, 50 volumes dissolving in 1 volume of water at 12° ; it is very soluble in turpentine.

116. Chemical Properties. — Ozone is a more active form of oxygen. What, then, is the exact relation of these two substances? When the chemist carefully examines the formation of ozone from ordinary oxygen, he finds that the latter absorbs energy and that the action is *reversible*:

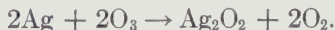


This means that 3 gram-molecular weights (96 g.) of oxygen absorb 61,400 cal. in passing into 96 g. (2 gram-molecular weights) of ozone. As the action is reversible, 96 g. of ozone liberate 61,400 cal. in passing over to the same weight of oxygen. It should be known, also, that 3 volumes of oxygen yield 2 volumes of ozone; but the 2 volumes of ozone weigh the same as 3 volumes of oxygen, for the density of the former gas is 1.5 that of the latter.

Ozone is therefore a more energetic form of oxygen, and it may be formed by heating oxygen to very high temperatures. At $4,500^{\circ}$, the percentage of ozone formed is 16.5, at equilibrium.

Ozone is unstable (endothermic substance); therefore liquid ozone must be handled with care, for it may explode. Ozone is decomposed immediately into oxygen, at $250-300^{\circ}$.

Ozone is a powerful oxidizing agent; it attacks mercury, and even silver in the presence of a trace of silver oxide. Ozone decomposes unless it is mixed with oxygen. In acting as an oxidizing agent the general rule is that ozone (O_3) breaks down, forming oxygen (O_2). Thus, the following equation shows the oxidation of silver to silver peroxide:



Potassium iodide — starch paper is colored blue by ozone, due to the liberation of iodine:



Ozone bleaches (oxidizes) many organic dyes, as may be shown by bubbling it through a solution of indigo. In preparing ozone, rubber connections must be avoided, for rubber is quickly destroyed.

117. Allotropy. — The relation of ozone to oxygen has been discussed. Here is a case of two different substances containing only one elemental form of matter. In other words, there are two forms or modifications of the element oxygen. Substances thus related are called *allotropic*. That property by virtue of which one substance may exist in two or more forms possessing different amounts of available energy (hence different properties) is called **allotropy** (Greek, meaning *another way* or *mode*). Allotropic forms, then, possess different amounts of available energy, hence they exhibit different properties. There are a number of common examples of allotropic forms: *e.g.*, charcoal (pure), the diamond, and graphite are carbon; white (yellow) and red phosphorus; rhombic and monoclinic sulfur; gray and white tin. The less common form is sometimes called an “allotropic modification” of the other.

Not only is allotropy applied to the elements, but also to those modifications of inorganic compounds which differ principally in physical properties. Thus, the minerals calcite and aragonite are calcium carbonate (CaCO_3), but they possess different physical properties. There are two forms of solid mercuric iodide, which may be prepared as red tetragonal crystals and as yellow rhombic crystals. If the red form be heated to 126° , it changes to the yellow variety, which, on cooling, changes to the red. This relationship may be shown thus:



118. Uses of Ozone. — The chief use of ozone is for the purification of water, mostly in European cities. The gas is bubbled through the filtered or settled water, in a long column. It is also used for the purification of the air of railway tubes, as well as animal houses of zoölogical gardens; for bleaching oils, waxes, ivory, flour and starch, etc. Ozone is a good deodorizer, and it oxidizes moist organic matter to harmless substances.

119. **Catalysis.** — The presence of small quantities of certain substances alters the speed of many chemical actions. Thus, the presence of such oxides as manganese dioxide, ferric oxide, and copper oxide accelerates the decomposition of potassium chlorate; finely divided manganese dioxide will cause the rapid evolution of oxygen from hydrogen peroxide; and ozone is changed into oxygen when brought in contact with platinum black. In none of these cases is the metallic oxide or the metal permanently changed. This sort of action is sometimes termed **contact action**, because the substances appear to act by contact. Berzelius proposed the name catalytic action or **catalysis** (Greek, meaning *breaking down*, or *decomposition*).

The substance which alters the speed of a chemical action is termed a catalyst.

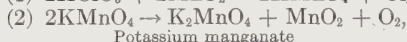
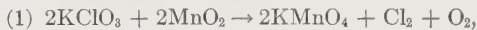
W. Ostwald compares the action of a catalyst with the influence of oil on the wheels of a machine, for the catalyst is unchanged in weight and composition at the end of a chemical action, just as the lubricating oil is not burned up or changed chemically by the machine when in operation. As a rule, a chemical change is not started by a catalyst; it merely affects the rate or speed of change.

The terms *positive catalyst* and *negative catalyst (inhibitor)* are employed. To illustrate, water functions as a positive catalyst in many chemical reactions; indeed, it is doubtful if any chemical change will take place in the complete absence of water. Perfectly dry charcoal will not burn in perfectly dry air or oxygen, and perfectly dry hydrogen and oxygen will not combine to form water; but when a trace of water is introduced, the action proceeds vigorously. Hydrogen peroxide tends to break down, yielding water and oxygen; to lessen its decomposition a small quantity of acetanilide is added as a negative catalyst or an inhibitor.

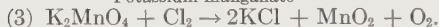
Enzymes, or ferments, are present in all living organisms. The catalytic effect of yeast upon dough is perhaps the earliest recorded example of the phenomenon of catalysis. Enzymes play an essential part in life-processes. For instance, they are very important in digestion, fermentation, oxidation, and decay. Enzymes work independently. Thus, one splits starch, another splits proteins, and still another splits fats.

Many important manufacturing operations, such as the contact process for sulfuric acid, the synthetic (Haber) process for ammonia, and the hydrogenation of oils, depend upon catalysis. It is destined, therefore, to play a greater rôle in chemistry, for it means the speeding up and the cheapening of many operations.

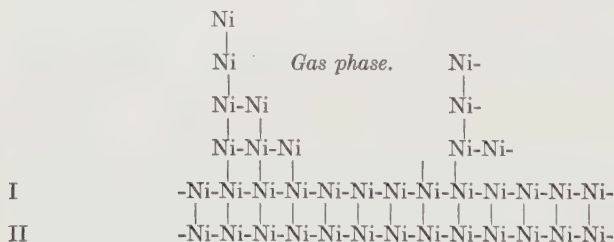
Not much is known about the precise way in which catalysts do their work. In one type of chemical change there is evidence that the catalysts form unstable intermediate compounds which break down, leaving the catalyst unchanged. In the case of potassium chlorate and manganese dioxide there is evidence that manganese dioxide reacts with potassium chlorate to form potassium permanganate (KMnO_4), the latter compound then decomposing to form manganese dioxide and other substances. The following equations have been suggested for the chemical changes:



Potassium manganate



Professor Hugh Stott Taylor and his co-workers of Princeton have carried out a great deal of experimental work on catalysis, and a most interesting theory of the catalytic surface has been developed. It has been discovered that a catalyst surface, such as that of nickel, shows a *varying capacity* to adsorb gas and to promote catalytic change. While the body of a granule of the catalyst is crystalline, *i.e.*, has an ordered arrangement of atoms, it appears that here and there, on the surface of a mainly crystalline granule, there are groups of atoms in which the process of crystallization is not yet complete. The following representation of a cross-section of a minute portion of such a granule of nickel may serve as an illustration of such an incomplete stage in the crystalline process:



GRANULE PROPER

Diagrammatic representation of a portion of a granule surface in cross-section.

The atoms in the second layer (II) of the granule proper will be surrounded on six sides by other nickel atoms. The atoms in the surface layer will be surrounded by neighboring metal atoms in all directions except that toward the gas phase. The degree of constraint or saturation imposed by this orderly arrangement of atoms becomes progressively less and less as we proceed outward from the granule proper (I and II) toward the most exposed metal atoms. Thus, the uppermost nickel atoms in the above representation suffer only one constraint by reason of their single attachment to the nickel atom immediately below. Further, we may note that the atoms in the edge of a granule have one less degree of saturation than those in the surface proper; atoms at a corner have two less than those in the surface and one less than those at an edge. A surface of a granule may thus be regarded

as composed of atoms in varied degrees of saturation by neighboring metal atoms, varying from those one degree less saturated than interior atoms to those which are only held to the solid surface by a single constraint. It is by this constraint alone that these outermost atoms differ from gaseous metal atoms. A gaseous atom of nickel can combine with four molecules of carbon monoxide to form nickel carbonyl. It is not therefore improbable that exposed nickel atoms, held by only a single valence to the solid surface, shall have a capacity to attach to themselves or adsorb three molecules of carbon monoxide or, alternatively, three molecules, the bonding between which and the nickel atoms is identical with that obtaining in nickel carbonyl. With the metal attached to the granules by two constraints, two such molecules might be adsorbed. This concept introduces a mechanism whereby both the constituents of a hydrogenation process (127) may be attached to one and the same nickel atom.¹

Likewise, the activation of platinum and silver gauzes in catalytic oxidation is believed to be due to a production, by disintegration of the plane-surfaced wire, of metal atoms to a large degree unsaturated and detached from the normal crystal lattice of the metal, and capable of adsorbing several molecular reactants. The notion that certain metal atoms are more or less detached from the normal crystal lattice accords with other observations. These outer atoms should have a greater freedom of motion, and should be relatively sensitive to the influence of thermal change. In the case of nickel, for example, the metal is very sensitive to the influence of heat, whereby marked sintering occurs, indicating that the process of crystallization is incomplete. It is well known that certain metal catalysts, *e.g.*, platinum in the contact process for sulfuric acid, are easily "poisoned" by foreign matter, and their action thereby inhibited. According to the Princeton view, "it is the less saturated catalyst atoms in the surface which will be the preferred positions of attachment of adsorbed catalyst poisons. As the quantity of poison increases, more and more of the surface atoms will be covered with poison. In the final issue the whole surface will be covered."

Catalysis may be illustrated by the following *experiments*:

(1) A few grams of potassium chlorate are just melted in a hard-glass tube, and a little manganese dioxide added. Oxygen may be tested for with a glowing splint.

(2) A pinch of manganese dioxide is added to 10–15 cc. of ordinary hydrogen peroxide solution contained in a test-tube. Oxygen is rapidly evolved, as may be shown by the introduction of a glowing splint.

EXERCISES

1. What position does oxygen occupy in the Periodic System? Write the formulae for ten oxides; also for ten analogous sulfides.

2. Give the history, occurrence, preparation, physical properties, chemical properties, and uses of oxygen.

¹ [That is to say, the loose atoms at the surface of the catalyst serve as links in effecting a union between atoms or molecules of substances which do not readily react or unite in the absence of the catalyst.]

3. Outline the classical experiment of Lavoisier which proved that oxygen is a component of the air.

4. Consult a work of reference and note some of the important discoveries made by Scheele.

5. How do you account for the fact that the oxides of the precious metals yield oxygen when heated, while calcium oxide and magnesium oxide do not?

6. Explain how industrial oxygen is produced.

7. Define and also illustrate the following terms: combustion, oxidation, oxidizing agent, kindling temperature, burning temperature, heat of combustion, exothermic change, endothermic change, oxidizing agent, reducing agent, and explosion.

8. Point out the great rôle played by oxygen in nature and in the arts.

9. Outline the Phlogiston Theory. How was it overthrown?

10. Mention some conditions which influence speed of oxidation.

11. Explain the following: (1) rusting of metals; (2) the production of animal heat; (3) spontaneous combustion; (4) why fine iron filings burn better than coarse filings.

12. Give the preparation, properties, and uses of ozone. Explain just how it is related to oxygen. Define and illustrate allotropy.

13. If a liter of oxygen at S.T.P., weighs 1.429 g., while one of ozone weighs 2.1435 g., find the volume occupied by one gram-molecular weight of each substance, and the weight of 3 liters of oxygen and of 2 liters of ozone. What is the relative density of ozone (oxygen = 1)?

14. J. L. Soret showed that the diminution in volume when ozone is absorbed from ozonized oxygen by oil of turpentine is double the increase in volume observed when ozone is reconverted into oxygen on heating. Explain the significance of this fact.

15. If 100 cc. of water at 12° C. dissolve 50 cc. of ozone, under atmospheric pressure, what volume of the gas will be taken up from a stream of oxygen containing 10 per cent of ozone? (See Dalton's Law.)

16. 100 cc. of ozonized oxygen were shaken with oil of turpentine and the volume of residual gas measured 88 cc. What expansion should occur when 100 cc. of the original gas is heated to 300° C.? (*Note. — Assume that all volumes are measured at S.T.P.*)

17. How would you detect the presence of ozone?

18. Can you suggest any reason as to why the ozone molecule is less stable than the carbon dioxide molecule?

19. Define and illustrate catalysis. Why is catalysis so important? What are enzymes?

20. When a mixture of potassium chlorate and manganese dioxide is heated for the preparation of oxygen, how would you show experimentally that the dioxide is not permanently changed?

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CHAPTER VII

HYDROGEN. VALENCE. CALCULATIONS

HYDROGEN. $H = 1.008$

120. **History.** — Paracelsus (1493-1541) knew that iron and sulfuric acid interact to form a gas. He said that when the acid and iron interact, “an air arises which bursts forth like the wind.” In 1700 N. Lemery showed that a mixture of hydrogen and air exploded on the application of a light. Cavendish first ascertained the true nature of the gas in 1766, and he called it “inflammable air.” In 1781 Cavendish proved that hydrogen burns in air to form nothing but water. Lavoisier (1783) named the gas **hydrogen** (Greek, meaning *water-producer*).

121. **Occurrence.** — (1) *Free State.* Mixed with other gases, hydrogen occurs in certain volcanic emanations; it is present in the intestinal gases of many animals; the gas is given off by the oil wells of Pennsylvania; a very small quantity is present in the atmosphere; it is found in the carnallite of the Stassfurt potash mines and in certain meteorites; the spectroscope shows that hydrogen is present in the sun, many stars, and nebulae. The chromosphere of the sun owes its name to the fact that as seen momentarily, during a total eclipse, it is of a bright scarlet caused by glowing hydrogen. These huge red streamers sometimes extend 500,000 miles from the sun's disc.

(2) *Combined Hydrogen.* Water contains 11.19 per cent of hydrogen; it is an essential constituent of all acids, hydrocarbons, and vegetable and animal matter; it is also a constituent of very many of the carbon compounds, such as the alcohols, ethers, sugars, starch, and cellulose.

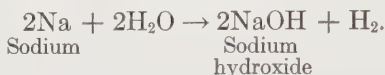
122. **Preparation.** — Hydrogen may be obtained from water, acids, and bases.

I. Hydrogen from Water.

(1) *By the interaction of the active metals (the alkali and alkaline earth metals) and cold water.* Thus, when a piece of clean sodium about the size of a pea is thrown upon water, hydrogen is liberated, accompanied by a hissing sound and the evolution of heat. By introducing a small piece of sodium [Care!] into a test-tube filled with water and inverted over a vessel containing the latter substance, hydrogen may be collected and examined.

As the reaction is violent, *hydrone*, an alloy containing lead and 35 per cent of sodium, may be used instead of sodium. Sodium amalgam, prepared by dissolving sodium in mercury, also yields hydrogen when treated with water, but is much less active than metallic sodium.

The equation for the reaction is as follows:



The solution is alkaline, for it is soapy to the touch and turns red litmus blue.

The interaction of potassium and cold water is so violent that the escaping hydrogen ignites spontaneously, burning with a violet flame, due to the vapor of potassium. Calcium and cold water interact rather mildly:



Very finely divided magnesium also decomposes cold water slowly.

Magnesium amalgam (an alloy of magnesium and mercury)

interacts vigorously with cold water to yield hydrogen. When the two metals are rubbed together in a mortar to form the amalgam, the oxide film is removed from the magnesium, thus exposing its surface to the action of water.

(2) *By the interaction of certain metals and water at high temperatures.*

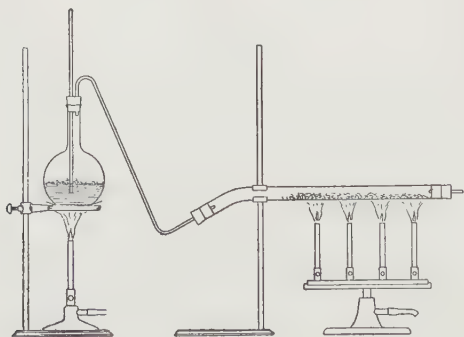


FIG. 60.

When steam is passed over hot magnesium, as shown in Fig. 60, hydrogen is liberated:



The metal burns (oxidizes) producing light, and water is reduced. MgO is formed instead of $\text{Mg}(\text{OH})_2$, for all common hydroxides, except NaOH and KOH, are decomposed at high temperatures: e.g., $\text{Mg}(\text{OH})_2 \rightleftharpoons \text{MgO} + \text{H}_2\text{O}$.

Zinc and steam are analogous to magnesium and steam. Steam is also decomposed by heated iron, aluminium, nickel, cobalt, lead, and tin, but not by copper or the precious metals. When steam is passed over highly heated iron, hydrogen and magnetic oxide of iron are formed. This action is reversible, as we shall see shortly, for by passing hydrogen over hot Fe_3O_4 , iron is liberated:



Large quantities of hydrogen for commercial purposes are manufactured by this method.

II. Hydrogen from Acids.

(1) *By the interaction of metals and diluted acids.* The active and moderately active metals, such as Na, Mg, Zn, Fe, and Al, interact with certain diluted acids, such as hydrochloric and sulfuric, to form hydrogen. The metal displaces hydrogen.

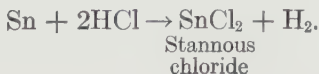
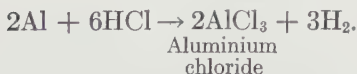
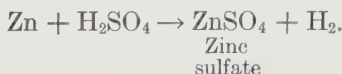
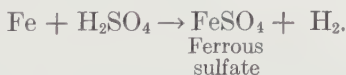
The less active metals, such as Cu, Hg, Ag, Au, and Pt, do not interact with acids to form hydrogen.

Nitric acid cannot be used because of the fact that it is an active oxidizing agent.

The metals most commonly used are zinc and iron. Magnesium, however, is more active. Hydrochloric and sulfuric acids are generally used.

Granulated zinc is employed for general laboratory work. A convenient and safe generator consists of a bottle of 100–150 cc. capacity, fitted with a funnel-tube and a delivery tube for collecting the gas over water. All joints must be fitted carefully, for hydrogen mixed with air explodes violently when ignited. Granulated zinc is treated with either dilute sulfuric or hydrochloric acid.

The following are typical equations:



Note that *diluted acids must be used*. To illustrate, if zinc be dissolved in concentrated sulfuric acid, the acid suffers reduction (loses oxygen), hydrogen sulfide (H_2S) being formed:



Sulfur and sulfur dioxide may also be formed, since they are reduction products of H_2SO_4 .

For preparing large quantities in the laboratory, *Kipp's apparatus* (Fig. 61) is very convenient. It is easy to regulate the supply of gas, for when the stopcock is closed the gas accumulates in the middle globe, which forces out the acid.

Hydrogen generated by the interaction of zinc or iron with acids contains small quantities of impurities, which may be removed by passing the gas through certain solutions.

When pure zinc is treated with dilute sulfuric or hydrochloric acid, hydrogen is formed very slowly. The action can be accelerated by bringing the zinc in

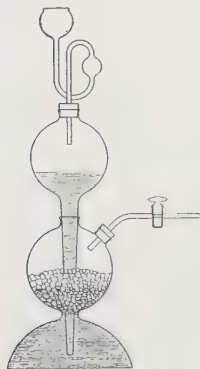


FIG. 61.

contact with an inactive metal like copper or platinum, for an electrical couple is formed (617). Commercial zinc contains impurities, which accelerate the action for the reason just mentioned.

(2) *By the electrolysis of diluted acids.* Acids are made up of a positive radical (hydrogen) and a negative radical: for example, hydrochloric acid $\text{H}(\text{Cl})$, sulfuric acid $\text{H}_2(\text{SO}_4)$, acetic acid $\text{H}(\text{C}_2\text{H}_3\text{O}_2)$. When an acid is subjected to electrolysis, hydrogen appears at the cathode (negative).

When an electric current is passed through water containing a little sulfuric acid, hydrogen and oxygen are liberated. Inasmuch as all acids contain hydrogen, the element may be liberated at the cathode by passing an electric current through a solution of any acid (Fig. 62). This method yields hydrogen of a high degree of purity.

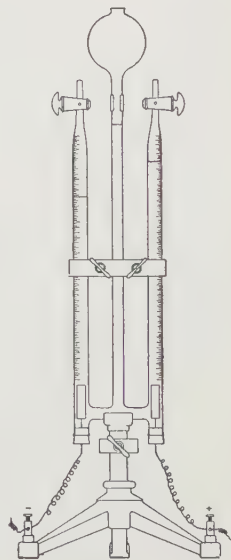


FIG. 62.

The process of decomposition by the use of the electric current is called **electrolysis** (Greek, meaning *decomposition by electricity*).

III. Hydrogen from Bases.

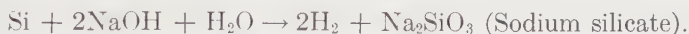
Hydrogen can be prepared by treating certain metals with certain bases (alkalies). Thus, aluminium turnings may be boiled with a solution of sodium hydroxide:



or, zinc and solid sodium hydroxide may be heated:



A method for preparing hydrogen, known as the *silicol process*, is based upon heating powdered silicon, or an alloy of silicon and iron, with a concentrated solution of sodium hydroxide:



Hydrogenite, a mixture of ferrosilicon and sodium hydroxide, is also a source of hydrogen.

IV. Industrial Preparation of Hydrogen.

Hydrogen is now prepared on a large scale, for it has a number of industrial uses. Many processes are available, but some of these are manufacturing processes in which hydrogen is obtained as a by-product. Some of the most important methods are as follows:

(1) *The Iron Contact (Lane) Process.*

Steam is first passed over red-hot iron:



In the course of time the reaction stops, due to the formation of a protecting film of oxide. Water gas (hydrogen + carbon monoxide, formed by passing steam over red-hot coke) is then turned on, which reduces Fe_3O_4 to iron. Water gas is then shut off and more steam turned on. By the alternate use of steam and water gas, a small quantity of iron can be used almost indefinitely.

In this connection it is of interest to note that in the *Bergius process* iron and water are heated in a bomb to 300° under a pressure of 100 atmospheres:



(2) *By the Electrolysis of Water.* This process is also carried out on a large scale. Sodium hydroxide is dissolved in the water to make it a conductor. The gas is of a high degree of purity.

(3) When a solution of common salt (NaCl) is decomposed by means of the electric current, caustic soda (NaOH) and chlorine are obtained, together with hydrogen (a by-product):

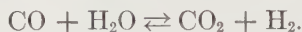


(4) *From Water Gas.* (a) Water gas is first manufactured by passing steam over coke (carbon) at $1,000^\circ \text{C}.$:



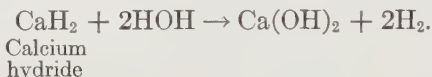
By producing a low temperature and applying pressure, the carbon monoxide liquefies, leaving the hydrogen as a gas.

(b) Water gas is manufactured as above, and the hydrogen and carbon monoxide, along with an excess of steam, are passed over oxide of iron (a catalyst) at 500° . CO is oxidized to CO_2 :



The carbon dioxide is then removed, leaving the hydrogen.

(5) *Hydrogen for military purposes has been prepared by treating calcium hydride (hydrolite) with water:*



The method is expensive, but it is easy to transport the solid, calcium hydride.

123. Physical Properties. — Hydrogen is a colorless, odorless, and tasteless gas. It is slightly soluble in water, about 2 volumes of the gas dissolving in 100 volumes of water at 15° .

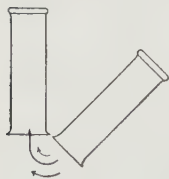


FIG. 63.

One liter of hydrogen weighs, at S.T.P., 0.08987 g. (approximately 0.09 g.). Its specific gravity with reference to air is 0.06949, which means that air is about 14.4 times as heavy as hydrogen. Hydrogen is the lightest known gas; its extreme lightness may be shown (1) by pouring the gas upward (Fig. 63); (2) by allowing it to flow into a large inverted beaker or flask suspended from one arm of a balance which has been carefully counterpoised; and (3) by filling balloons or by blowing soap-bubbles.

Hydrogen liquefies at about $-240^\circ (\text{C.T.})$ and under a pressure of about 15 atmospheres (C.P.). Liquid hydrogen is colorless, boils at -252.5° , and has a density of 0.07. When liquid hydrogen is

allowed to evaporate rapidly, it freezes to a white solid, melting at -258.9° (Travers).

All other known gases, except helium, solidify easily when led into a vessel surrounded by liquid hydrogen.

Hydrogen is absorbed by many metals. Graham proposed the name **occlusion** (Latin, *occludo*, I shut up) for this phenomenon. Palladium, platinum, gold, iron, nickel, and cobalt are among the metals which absorb the gas. Palladium black at ordinary temperatures absorbs between 800 and 900 volumes of hydrogen; platinum in fine powder absorbs about 50 volumes; iron, 19; and silver, none.

When hydrogen is allowed to impinge upon finely divided platinum exposed to the air, so much heat is generated by the absorption of the gas that it ignites. This is the principle involved in the construction of the **Döbereiner lamp** and certain automatic cigar lighters.

Hydrogen diffuses more rapidly than any other gas (50).

124. Chemical Properties. — Hydrogen does not unite with as many of the elements as does oxygen. Some binary compounds of hydrogen, such as water (H_2O), ammonia (NH_3), and hydrochloric acid gas (HCl), are of the greatest importance. Binary compounds of hydrogen are frequently called **hydrides**; *e.g.*, NaH , sodium hydride; NH_3 , nitrogen hydride (ammonia).

The molecule of ordinary hydrogen is diatomic (H_2) and is very stable, even when heated. Irving Langmuir produces **atomic hydrogen** (H) by passing ordinary hydrogen (H_2) into an electric arc. In dissociating into monatomic hydrogen, the action is strongly endothermic:



When monatomic hydrogen is burned, it yields a flame with an extremely high temperature, even higher than the oxyacetylene flame, which is of great value in welding metals. Minute flames of atomic hydrogen can be produced and maintained, thus making it possible even now to weld sheets of metal as thin as five one-thousandths of an inch.

According to Langmuir, iron can be melted in the flame of atomic hydrogen without contamination by carbon, oxygen, or nitrogen. As atomic hydrogen has reducing action, alloys containing chromium, aluminium, silicon, or manganese can be melted without fluxes and without surface oxidation.

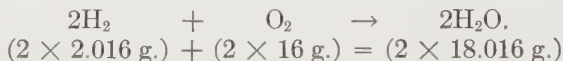
When molecules of hydrogen collide with mercury atoms which

have been "excited" by a radiation emitted by a cooled mercury arc, atomic hydrogen is formed. Hydrogen thus formed is exceedingly active. For instance, it will reduce metallic oxides at room temperature, react with oxygen to form hydrogen peroxide and water, and with carbon monoxide to form formaldehyde (CH_2O).

J. J. Thomson, in 1913, produced **triatomic hydrogen** (H_3) by bombarding potassium hydroxide with cathode rays. It also has been produced by the action of α -particles (66) on hydrogen (H_2) at reduced pressure. H_3 is very active. Thus, it combines with mercury, and when exposed to the light of burning magnesium it unites with oxygen. We thus see that there are allotropic forms of hydrogen (117).

I. Hydrogen and the Non-metals.

Hydrogen burns to form water:



That water is the product of combustion, may be shown by allowing a jet of burning hydrogen to impinge upon a glass vessel containing cold water. The gas is dried before burning by passing it through a tube containing calcium chloride.

When hydrogen burns, a large quantity of heat is liberated (exothermic action). When hydrogen and oxygen are burned



FIG. 64.

in the **oxyhydrogen blow-pipe**, an intense heat is produced. By means of this flame, platinum may be readily melted and a steel

spring or wire burns in it brilliantly. In a closed space the temperature may rise to over $2,500^\circ \text{C}$. The structure of the burner is shown in Fig. 64. The oxyhydrogen blowpipe was invented by Robert Hare of Philadelphia in 1801.

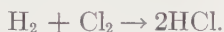
The oxyacetylene blowpipe or torch has partially displaced the oxyhydrogen blowpipe. Acetylene gas is substituted for hydrogen, and the temperature obtained is higher (about $3,300^\circ \text{C}$). As this flame has reducing action, it is very suitable for welding materials.

When hydrogen and oxygen are mixed, they combine very slowly at 180° , and when exposed to bright sunlight at ordinary temperature. When the moist gases are mixed, they explode at a temperature not under 550° . Increase of temperature has,

therefore, a very marked effect upon the speed of chemical action. H. B. Baker has shown that perfectly dry hydrogen and oxygen will not combine.

When finely divided platinum is introduced into a cold mixture of hydrogen and oxygen, the speed of combination is so accelerated by the metal (a catalyst), that an explosion follows (105).

Hydrogen combines directly with the halogens:



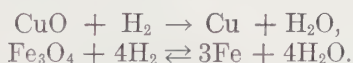
It also combines with nitrogen to form ammonia (NH_3), and with sulfur to form hydrogen sulfide (H_2S).

II. Hydrogen and the Metals.

Hydrogen combines directly with the more active metals to form hydrides. Thus, NaH , sodium hydride; CaH_2 , calcium hydride.

III. The interaction of Hydrogen and Compounds.

Hydrogen is a powerful reducing agent; it reduces the heated oxides of many of the metals; also some of the compounds of chlorine:



Note that these actions are the converse of oxidation. It is also of interest to note that *oxidation always accompanies reduction*.

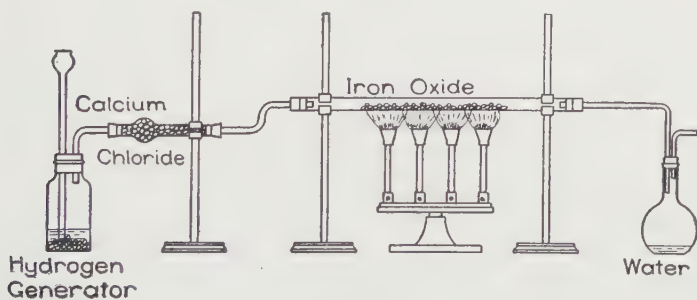


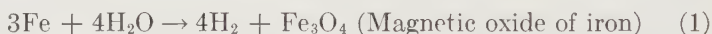
FIG. 65.

The reducing action of hydrogen can be shown by passing dry hydrogen from a Kipp generator over copper oxide contained in a small porcelain boat placed inside a hard-glass tube. Copper (red) is left in the boat, and water condenses upon the cooler part of the tube. It may also be shown by passing hydrogen over a hot oxide of iron, such as Fe_3O_4 . (Fig. 65.)

Hydrogen occluded by palladium is especially active as a reducing agent, readily reducing ferric salts to ferrous salts, nitrates to nitrites and ammonia, and chlorates to chlorides, etc.

125. Reversible Actions. — We have seen that mercuric oxide (HgO) may be decomposed into mercury and oxygen, and that mercury will combine with oxygen to form mercuric oxide (96); also, that hydrogen can be produced by passing steam over red-hot iron, and oxides of iron can be reduced to the metallic state by means of hydrogen. In other words, these are reversible or opposed actions.

By choosing suitable conditions, many chemical reactions may be made to proceed in either direction. Thus, when steam is passed over red-hot iron, the chemical change may be represented as follows:



When hydrogen is passed over heated magnetic oxide of iron we have:



Equation (2) is just the reverse of equation (1). In order to complete the reaction represented by (1), an excess of steam is employed, the hydrogen being allowed to escape. The reverse action (2) may be completed by passing a large excess of hydrogen over the hot oxide of iron, the steam being removed or condensed.

If, however, we heat either pair of substances — iron and steam or oxide of iron and hydrogen — in a closed vessel, the action cannot be completed in either direction; for the two actions oppose each other:



Under certain conditions, *e.g.*, at 440° , a condition of apparent rest, or equilibrium, would be reached. This is the case when the speed of the action to the right is just equal to the speed of the action to the left. At equilibrium there is no further change in the concentrations or relative quantities of the reacting substances.

126. The Order of Activity of the Metals. — The alkali and the alkaline earth metals are the most active, and the noble metals the least active. As the result of experiment, the metals have been arranged in a series in which each element is less active than the element or elements preceding it.

Some of the more common metals, together with hydrogen, are given in the following table:

General Remarks on the Metals

<i>Order of Activity of Metals</i>	
Potassium	(1) All above hydrogen displace this element from acids.
Sodium	(2) Potassium displaces hydrogen from water violently, sodium and calcium less so, magnesium slowly acts on boiling water, but, like iron, it interacts with steam vigorously at a high temperature.
Calcium	
Magnesium	(3) When the metals are heated with pure oxygen, all unite with it down to silver. Potassium and sodium quickly tarnish in air or oxygen at ordinary temperatures.
Aluminium	
Manganese	
Zinc	
Iron	
Nickel	(4) When the oxides of the metals are heated, those from mercury through gold lose their oxygen.
Tin	
Lead	(5) When the oxides of the metals are heated and hydrogen passed over them, they are reduced (lose oxygen) from iron through gold, leaving the free metal.
HYDROGEN	
Copper	
Antimony	
Mercury	
Silver	(6) The more active metals form, as a rule, the most stable compounds.
Platinum	
Gold	(7) The metals below hydrogen are the ones found in the native (free) state.

127. Uses of Hydrogen. — In recent years, the use of hydrogen on an industrial scale has increased very rapidly. During the Great War enormous quantities were used for inflating balloons and airships. When certain oils, *e.g.*, cottonseed oil, are treated with hydrogen in the presence of such catalysts as nickel and nickel oxide, the unsaturated oil (liquid fat) combines with the gas to form a solid fat: *e.g.*, large quantities of "Crisco" are manufactured from vegetable oils. Hydrogen is used in the oxyhydrogen blowpipe, but acetylene is rapidly displacing it. The gas is also used in the manufacture of synthetic ammonia (NH_3) and methyl alcohol (CH_4O), as a reducing agent, etc. Large quantities of hydrogen mixed with carbon monoxide are used as fuel (see Water Gas).

The ZR-3 (now the *Los Angeles*) was originally inflated with hydrogen. This huge Zeppelin reached Lakehurst, New Jersey, October 15, 1924, only 81 hours after sailing from Friedrichshaven, Germany, 5,000 miles away. Subsequently it was inflated with helium gas, which has about 92 per cent of the lifting power of hydrogen for a balloon floating in the air.

These equations, which have been constructed by chemists to represent the weight relations of the various substances concerned, show that when gram-atomic weights of different metals are dissolved in an acid, different weights and volumes of hydrogen are liberated. In other words, an atom of a metal is capable of displacing a definite number of hydrogen atoms. Sodium, therefore, has a valence of 1, magnesium 2, and aluminium 3.

W. A. Noyes describes a very helpful *experiment* on valence as follows:

"If 23 milligrams of sodium, 24 milligrams of magnesium, and 27 milligrams of aluminium are allowed to act on hydrochloric acid in such a way that the hydrogen is generated in separate tubes, it will be found that the sodium will give about 11 cc. of hydrogen, the magnesium 22 cc., and the aluminium 33 cc." (Fig. 66.) It follows from this experiment that sodium has a valence of 1, magnesium 2, and aluminium 3.

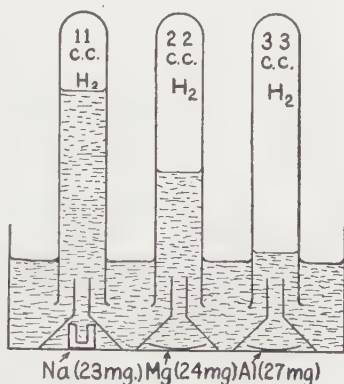


FIG. 66.

Valence may now be defined thus: **The valence of an atom (atomic weight) of an element is a whole number which expresses how many atoms (atomic weights) of hydrogen it can hold in combination or displace in a reaction.**

Compound radicals (131) frequently pass from compound to compound when chemical changes occur; they have, therefore, definite valences. Thus, the sulfate radical (SO₄) has a valence of two, for it is combined with two atoms of hydrogen in H₂SO₄. When sulfuric acid is treated with magnesium, hydrogen is evolved:



129. Marking Valences. — Valences of atoms and radicals are frequently marked thus: Na^I, Mg^{II}, Al^{III}, C^{IV}, O^{II}, (SO₄)^{II}, (OH)^I, (NO₃)^I.

Compounds may be written as follows: Na^ICl^{II}, Na₂IO^{II}, Al₂^{III}O₃^{II}, C^{IV}O₂^{II}, Al^{III}Cl₃^I, Mg^{II}IO^{II}, P₂^VO₅^{II}.

The atoms of the elements that combine to form a binary compound must have identical total valences, one being positive and the other negative: *e.g.*, in Al₂^{III}O₃^{II} the total valence of Al₂^{III} is 2 × III = 6, and that of O₃^{II} is 3 × II = 6.

Two atoms of aluminium are equivalent to three of oxygen. In $P_2^{VO_5^{II}}$ the total valence of the atoms of each element are identical, — $5 \times 2 = 10$.

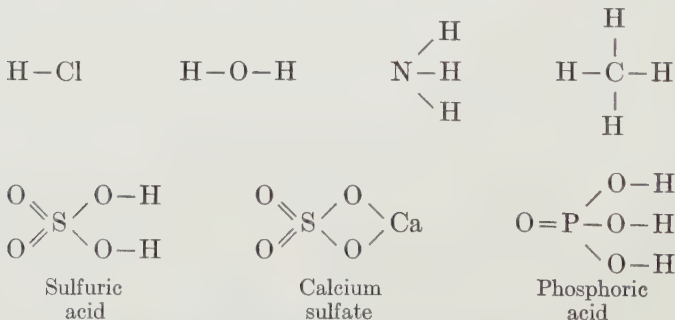
It may be stated, in general, that a compound is composed of elements which are, relatively to one another, either positive or negative. Thus, in the above compounds the valence of the first element is positive. Broadly speaking, the metals and hydrogen are positive, while non-metals are negative. As previously stated, however, the terms electropositive and electronegative are relative: for example, in PCl_3 phosphorus is positive, but in PH_3 (or H_3P) hydrogen is positive and phosphorus negative. In CO_2 carbon is positive as related to oxygen.

The sum of the positive and negative valences of an element does not exceed 8 (89), and in writing compounds the algebraic sum of the positive and negative valences is zero.

Thus, in $CaCO_3$, Ca^{II} and C^{IV} are positive, while O^{II} is negative. The sum is $(2 + 4) - (2 \times 3) = 0$ (see rule of equi-valence). In $KMnO_4$, K^I and Mn^{VII} are positive and O^{II} is negative. The sum is $(1 + 7) - (2 \times 4) = 0$.

The valence of the central element in compounds similar to $CaCO_3$ and $KMnO_4$ may be obtained by finding the difference between the total valences of the elements on each side.

130. Structural, Graphic, or Constitutional Formulae. — We can represent formulae graphically or structurally by imagining that an atom has one or more bonds for holding on to other atoms, as many bonds or lines being drawn as the atom possesses valences:



In writing *electronic formulae* (89), dots may be used to represent bonds of the ordinary structural formulae: for example, H_2SO_4 and H_3PO_4 may be written thus:



The anions ClO_4^- , $\text{SO}_4^{=}$, $\text{PO}_4^{=}$, and $\text{SiO}_4^{=}$ may be represented by the general electronic formula



If X is chlorine, the ion has one negative charge; if X is sulfur, the ion has two negative charges; etc.

In calcium carbonate (CaCO_3), the solid is built up of a lattice of the ions Ca^{++} and $\text{CO}_3^{=}$. The carbonate-ion appears to have three oxygen atoms arranged symmetrically about the carbon atom, all being in the same plane:



In carbonates, therefore, the carbon atom does not appear to possess four valence bonds, as represented in the structural formula

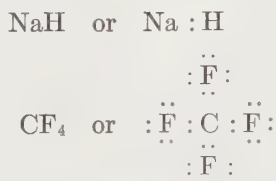


There is evidence which indicates *three types of linkages in molecules*, namely:

(1) **Polar or ionizable linkage.** This is the case when electrons are transferred from one atom to another: for example, in a salt, such as Li^+F^- or Na^+Cl^- , the ions are oppositely charged (88). This type of valence is known as **electrovalence**. The electronic formula for NaCl is $\text{Na} : \ddot{\text{Cl}} : .$

(2) **Non-polar linkage.** This type is also called non-ionizable or covalent linkage. It is due to the sharing of electrons, two to each link, between the atoms, and is especially prevalent in

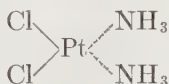
carbon compounds. This type of linkage may be illustrated by the following compounds:



(3) **The co-ordinate linkage of Werner.** This linkage is capable of uniting apparently saturated molecules.

A. Werner,¹ of Zürich, calls ordinary valence "primary." There is another type of valence which he terms "secondary." The latter is defined as a residual attraction which is left over after the primary valence is saturated.

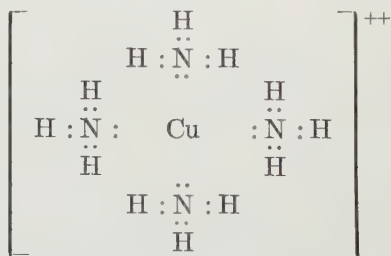
The theory of Werner has been very helpful in the study of metal-ammonia complexes. In one type of these complexes four radicals or elements are joined to a central atom, forming a non-ionizable "nucleus." These numbers are called "co-ordination numbers." The following substance is an example:



The primary valence is represented by the two bonds, and the secondary valence by the dotted lines.

The co-ordinate linkage of Werner is capable of uniting apparently saturated molecules.

Furthermore, certain bivalent metallic ions (*e.g.*, Cu^{++} and Zn^{++}) take on four NH_3 , forming complex ions, such as $\text{Cu}(\text{NH}_3)_4^{++}$, the cupric ammonia ion. The electronic formula of this complex may be written thus:



¹ "New Ideas in Inorganic Chemistry."

The number of groups or ions held by the positive ion is called the **co-ordination number**. Werner has observed that 4 is a prevalent co-ordination number.

131. **Valences of Elements and Radicals.** — The valence of an atom of an element or of a radical may be expressed by the use of a word either of Latin or of Greek origin. Thus, hydrogen is a univalent element, or monad; oxygen, a bivalent element, or dyad; etc.

VALENCE TABLE FOR THE MORE COMMON ELEMENTS AND RADICALS

I. Univalent (Monads):

+ : H, Na, K, Li, Ag, Cu(ous), Hg(ous), Au(ous), (NH₄).
 - : Cl, Br, I, F, (OH), (NO₃), (NO₂), (ClO₃), (C₂H₃O₂), (MnO₄)
 (in permanganates).

II. Bivalent (Dyads):

+ : Mg, Ca, Sr, Ba, Fe(ous), Zn, Cd, Cu(ic), Pb, Sn(ous), Hg(ic),
 Ni, Mn(ous), Pt(ous).
 - : O, S(in H₂S), (SO₄), (SO₃), (CO₃), (CrO₄), C₂O₄ (oxalate),
 (MnO₄) (in manganates).

III. Trivalent or Tervalent (Triads):

+ : Al, Fe(ic), Mn(ic), Cr(ic), Au(ic), B(in B₂O₃), N(in N₂O₃),
 P(in PCl₃), As(in As₂O₃), Sb(in SbCl₃), Bi(in BiCl₃).
 - : N(in NH₃), P(in PH₃), (PO₄), (PO₃), (AsO₄), (AsO₃), (BO₃).

IV. Quadrivalent (Tetrads):

+ : C(in CO₂), Si(in SiCl₄), S(in SO₂), Pb(ic), Mn(in MnO₂), Pt(ic).
 - : C(in CH₄), Si(in SiH₄).

V. Quinivalent (Pentads):

+ : N(ic), P(ic), As(ic), Sb(ic), Bi(in Bi₂O₆).

VI. Sexivalent (Hexads):

+ : S(in SO₃), Cr(in CrO₃).

VII. Septivalent (Heptads):

+ : Cl(in Cl₂O₇), Mn(in Mn₂O₇).

VIII. Octavalent (Octads):

+ : Os (in OsF₈), Ru (in RuO₄).

The inactive elements of the atmosphere, such as helium and argon, have zero valence, for they do not combine with other elements.

The above table will be very useful for reference as the study of the elements and their compounds progresses.

132. **Multivalence.** — As previously pointed out and as may be seen by reference to the valence table, some elements have more than one valence. Thus, sulfur has no less than three

valences: $\text{H}_2\text{S}^{\text{II}}$, $\text{Si}^{\text{IV}}\text{O}_2$, $\text{S}^{\text{VI}}\text{O}_3$; iron has two valences — ferrous iron, Fe^{II} , and ferric iron, Fe^{III} :

FeO , ferrous oxide; FeCl_2 , ferrous chloride;
 Fe_2O_3 , ferric oxide; FeCl_3 , ferric chloride.

Iron, mercury, tin, phosphorus, nitrogen, arsenic, etc., form two series of compounds, — those with names ending in *-ous* and those ending in *-ic*. The former always contain less oxygen, chlorine, etc.

The electron theory may be applied to the explanation of the variable valence of elements, such as manganese, iron, chromium, and copper.

According to the Lewis-Langmuir theory the exterior electrons are arranged in successive shells, while according to Bohr¹ they revolve in successive orbits. The maximum numbers of electrons in the shells, according to Lewis, follow the mathematical series:

$$2 \times 1^2; 2 \times 2^2; 2 \times 3^2; 2 \times 4^2.$$

The *maximum number* of electrons in the several shells is, therefore, as follows:

First shell	2 electrons
Second shell	8 electrons
Third shell	18 electrons
Fourth shell	32 electrons

To illustrate, the electron structure of radium (at. no. 88) may be represented thus: 2, 8, 18, 32, 18, 8, 2; for zinc (at. no. 30), 2, 8, 18, 2; and for xenon (at. no. 54), 2, 8, 18, 18, 8.

It is assumed that the outermost shell of electrons cannot contain more than 8 electrons, while the next to the outermost cannot contain more than 18 electrons. Furthermore, Bury suggested that "during the change of an inner shell from a stable group of 8 to one of 18, or from 18 to 32, there occurs a transition series of elements which can have more than one structure." It is clear that this would account for the multiple valences of certain elements. In cases of this kind it is assumed that one or more added electrons have a tendency to go into the third shell, thereby increasing its electrons toward its maximum of 18. This is illustrated below, in which the different electron arrange-

¹As to "Types of Electron Orbits of the Elements," see *Radioactivity*, by Hevesy & Paneth, p. 70.

ments for the same element are given. The last number in each group of numbers represents the valence of the element.

Chromium (at. no. = 24) 2, 8, 8, 6 (*chromates*); 2, 8, 11, 3 (*chromic compounds*); 2, 8, 12, 2 (*chromous compounds*).

Thus, in potassium chromate, K_2CrO_4 , chromium has a positive valence of 6; in chromic chloride, $CrCl_3$, it has a positive valence of 3; and in chromous chloride, $CrCl_2$, the element has a positive valence of 2.

Similarly, the variable valence of manganese (at. no. = 25) may be shown:

Manganese, 2, 8, 8, 7 (*permanganates*); 2, 8, 9, 6 (*manganates*); 2, 8, 11, 4 (*manganites*); 2, 8, 12, 3 (*manganic compounds*); 2, 8, 13, 2 (*manganous compounds*).

(Write formulae to illustrate the several valences of manganese. Also, arrange the electrons of the iron and copper atoms so as to illustrate the two common classes of compounds of each element.)

133. Equivalent Weights. — Review equivalent weights (29). The equivalent weight of an element was defined as the weight of the element that combines with 8 parts by weight (grams) of oxygen.

By re-reading section 128, it will be seen that 1 gram-atomic weight (23 g.) of sodium displaces 1.008 g. (1 equivalent weight) of hydrogen, while 1 gram-atomic weight of magnesium displaces 2×1.008 g. (2 equivalents), and 1 gram-atomic weight of aluminium displaces 3×1.008 g. (3 equivalents). The equivalent weights of the four elements are as follows:

Hydrogen, H.....	1.008 g.
Sodium, Na.....	23.00 g.
Magnesium, Mg.....	12.16 g. (= 24.32 \div 2)
Aluminium, Al.....	9.00 g. (= 27.00 \div 3)

This means that 23 g. of sodium, 12.16 g. of magnesium and 9 g. of aluminium yield the same quantity of hydrogen (1.008 g.) when they are dissolved in an acid; that is to say, they are chemically equivalent to each other. It is clear, then, that there is a definite relation between the atomic weight and the equivalent weight of an element:

$$\frac{\text{Atomic Weight}}{\text{Valence}} = \text{Equivalent Weight}$$

The term equivalent weight may now be given the following definition:

The equivalent weight of an element is that weight of it which combines with or displaces 8 parts by weight (grams) of oxygen or 1.008 parts by weight (grams) of hydrogen, *i.e.*, one atomic weight of hydrogen.

134. **Nomenclature of Compounds.** — Review what has been said about the naming of binary compounds (40).

The following simple rules are to be followed in *naming salts*, which may be regarded as derivatives of acids:

(1) Salts of binary acids have names ending in **-ide**.

(2) If the acid contains three or more elements and its name ends in **-ous**, its salts have names which end in **-ite**.

(3) If the acid contains three or more elements and its name ends in **-ic**, its salts have names ending in **-ate**.

The acids containing chlorine serve admirably to illustrate the nomenclature of acids and their corresponding salts, as shown by the following table:

Name of Acid	Formula of Acid	Formula of Potassium Salt	Name of Salt
Hydrochloric	HCl	KCl	Potassium chloride
Hypochlorous	HClO	KClO	Potassium hypochlorite
Chlorous	HClO ₂	KClO ₂	Potassium chlorite
Chloric	HClO ₃	KClO ₃	Potassium chlorate
Perchloric	HClO ₄	KClO ₄	Potassium perchlorate

Note that the prefixes of acids are retained in naming their salts. The prefix **per** is used in naming the acid richest in oxygen, while **hypo** indicates the acid containing the least amount of oxygen.

Some contain more than three elements: thus, $\text{H}_3\text{AsO}_3\text{S}$ (Monothioarsenic acid) \rightarrow $\text{K}_3\text{AsO}_3\text{S}$ (Potassium monothioarsenate).

In case the acid contains sulfur or some other element instead of oxygen, the same rules are followed: for example,

H_3AsO_4 (Arsenic acid) \rightarrow Na_3AsO_4 (Sodium arsenate),

H_3AsS_4 (Thioarsenic acid) \rightarrow Na_3AsS_4 (Sodium thioarsenate),

H_2CS_3 (Thiocarbonic acid) \rightarrow K_2CS_3 (Potassium thiocarbonate).

CALCULATIONS

135. To Find the Percentage Composition from a Given Formula. —

Example. — Calculate the percentage composition of potassium chlorate, KClO_3 (atomic weights: $\text{K} = 39$, $\text{Cl} = 35.5$, $\text{O} = 16$).

The formula-weight (molecular weight) of potassium chlorate is the sum of the atomic weights, which is $39 + 35.5 + (3 \times 16) = 122.5$. This means, for example, that 122.5 g. of KClO_3 contain 39 g. of potassium, 35.5 g. of chlorine, and 48 g. of oxygen. The percentage of potassium is found thus:

$$122.5 : 39 = 100 : x; x = 31.84 \text{ per cent of potassium.}$$

The percentages of the other elements are found in a similar manner:

$$122.5 : 35.5 = 100 : y; y = 28.98 \text{ per cent of chlorine.}$$

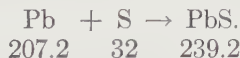
$$122.5 : 48 = 100 : z; z = 39.18 \text{ per cent of oxygen.}$$

$$x + y + z = 100 \text{ per cent; or, } (31.84 + 28.98 + 39.18) = 100 \text{ per cent.}$$

136. Calculations by the Use of Equations. — This may be illustrated by the following examples:

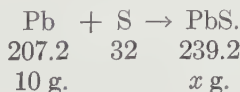
Example. — What weight of lead sulfide could be obtained by heating 10 g. of pure lead with sulfur in a covered crucible?

The following plan may be followed:

(1) Write the equation:**(2) Write under each symbol or formula the weight it represents:**

(3) Read the equation as follows: 207.2 parts by weight of lead combine with 32 parts of sulfur to form 239.2 parts of lead sulfide.

(4) Place the weight of the substance given in the problem under the formula of the substance and X under the formula of the substance sought:



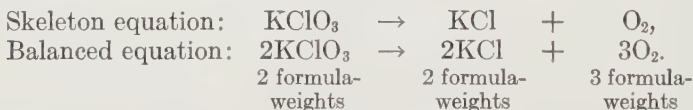
(5) The proportion may now be written thus:

207.2 : 239.2 = 10 : x , where x is the weight of lead sulfide.

$$x = \frac{239.2 \times 10}{207.2} = 11.544 \text{ g. of PbS}$$

The problem may also be solved as follows: If 207.2 g. of lead yield 239.2 g. of lead sulfide, 1 g. of lead yields $\frac{239.2}{207.2} = 1.1544$ g. of lead sulfide; therefore, 10 g. of lead yield $1.1544 \times 10 = 11.544$ g. of lead sulfide.

Example. — Given the weight of a liter of oxygen as 1.4290 g. at S.T.P., calculate the weight and volume of oxygen which can be obtained by heating 6 g. of potassium chlorate, KClO_3 . (Atomic weights: K = 39, Cl = 35.5, O = 16.)



$$\text{Relative parts by weight: } \left\{ \begin{array}{l} 2(39+35.5+3 \times 16) = 245 \\ 2(39+35.5) + 3(16 \times 2) = 149 + 96 \end{array} \right.$$

Now, these quantities are reaction-quantities, and they are always proportional to each other. We can express the actual weights concerned in any denomination we choose, such as grams, pounds, or tons. Let us take the gram as the unit of weight. We see from the equation that 245 g. (2 gram-molecular weights) of potassium chlorate yield 96 g. (3 gram-molecular weights) of oxygen; therefore, the weight of oxygen yielded by heating 6 g. of KClO_3 can be calculated thus:

$$245 : 96 = 6 : x; x = \frac{6 \times 96}{245} = 2.350 \text{ g.}$$

Since 1 liter of oxygen weighs 1.429 g., the volume occupied by 2.350 g. of the gas is equal to $2.350 \div 1.429 = 1.644$ liters at S.T.P. What volume would the oxygen occupy at 20° and 763 mm.?

The volume in liters of any gas may be found by dividing its weight by the weight of one liter of the gas, all weights being expressed in grams.

EXERCISES

1. Outline method of preparation for hydrogen (1) from cold water; (2) from steam; (3) from hydrochloric acid and aluminium; (4) by electrolysis; (5) from water gas. Write the equations showing the reactions which occur.

2. Name the common metals which will decompose water. Name several metals which will not decompose water. Can hydrogen be obtained by passing steam over heated copper? Explain.

3. How would you prove experimentally that the action of steam upon heated iron is reversible? What is meant by a state of chemical equilibrium?

4. Outline two good methods for producing hydrogen industrially.

5. A liter of hydrogen weighs 0.09 g., a liter of helium weighs 0.1782 g., and a liter of air, 1.293 g. Show that helium has about 92 per cent of the lifting power of hydrogen for a balloon floating in air.

6. Discuss the phenomenon of diffusion, and point out its importance in the atmosphere. State Graham's law of diffusion. The densities of hydrogen and of carbon dioxide stand to each other as 1 to 22. How many cc. of hydrogen would pass through a small orifice in the same time as 1 cc. of carbon dioxide?

7. Explain why finely divided platinum will cause a mixture of hydrogen and oxygen to explode.

8. Show by means of equations that hydrogen is a reducing agent.

9. Make a diagram to show the structure and operation of the oxyhydrogen blowpipe.

10. How may "atomic" hydrogen be produced, and what are its properties?

11. Arrange the following elements in the order of their chemical activity: Mercury, magnesium, calcium, gold, iron, hydrogen, copper, zinc, potassium, platinum, sodium, and silver. What general statements can you make concerning the order of these elements?

12. Discuss protective coatings of metals, illustrating by the following actions: magnesium + cold water; magnesium + dry steam; magnesium amalgam + cold water; aluminium + sodium hydroxide.

13. Outline the use of hydrogen in the production of solid fats from vegetable oils: *e.g.*, cottonseed oil.

14. Cite experimental proof to show that elements such as sodium, magnesium, aluminium, hydrogen, and chlorine have definite valences.

15. Mark the valences of the simple and compound radicals in the following substances: AlPO_4 , $\text{Mg}_3(\text{PO}_4)_2$, $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$, $(\text{NH}_4)_2\text{C}_2\text{O}_4$, K_2MnO_4 , NaMnO_4 , $\text{Sn}(\text{SO}_4)_2$, $\text{Ca}(\text{ClO}_3)_2$, Mn_2O_7 , and K_3AsS_4 . Name these compounds.

16. Correct the following formulae: CaNO_3 , PbCl , AgCl_2 , Mg_2CO_3 , $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2$, $(\text{NH}_4)_2\text{Cl}$, $\text{Ca}(\text{OH})$, SiO_3 , ZnS_2 , and PO_6 .

17. Write the formulae for the oxides, sulfides, chlorates, perchlorates, and arsenates of barium and of silver.

18. Calculate the percentage composition of zinc nitrate and of ammonium phosphate.

19. (a) What weight of hydrogen could be liberated by treating 12 g. of sodium with an excess of water? (b) What weight of sodium hydroxide would be formed? (c) What volume would the hydrogen occupy at S.T.P.?

(Note: 1 liter of hydrogen weighs 0.09 g.)

20. Can you suggest any reason as to why lithium and sodium, fluorine and chlorine (in halides) are all univalent?

21. Explain the variable valence of certain metals.

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CHAPTER VIII

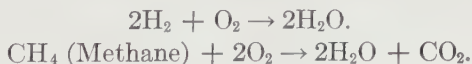
WATER AND HYDRATES. HYDROGEN PEROXIDE

137. **History.** — Cavendish, as previously stated, burned hydrogen in 1781 and obtained water as the sole product. He was so biased with the phlogistic theory, however, that he did not fully appreciate what he had discovered. Lavoisier (1783) repeated Cavendish's experiments, and gave the true explanation of the composition of water. .

138. **Occurrence.** — It is well known to all that water occurs in great abundance and very widely distributed. Water covers about three-fourths of the earth's surface, the greatest depth of the ocean being about 6 miles. Water vapor rises continuously from the surface of the sea and is condensed in colder regions, appearing as clouds and fog, or is precipitated as rain, snow, or sleet. Water vapor is an important component of the air. Even the "dry" land contains considerable quantities of water. Water also constitutes a large part of organisms. For example, about 70 per cent of the human body, 74 of eggs, 87 of milk, 92 of water-melons, 94 of tomatoes, and 95 per cent of cucumbers is water. The presence of water in organic matter may be shown by heating pieces of an apple or of a potato in a clean test-tube.

139. **Formation.** — Water is so abundant that it is not necessary to prepare it. Among the methods of formation are the following:

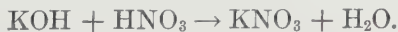
- (1) *By burning hydrogen or matter containing hydrogen:*



- (2) *By reducing heated oxides of metals:*



- (3) *By the interaction of a base and an acid:*



140. **Physical Properties.** — Pure water is a clear, tasteless, odorless liquid; it is colorless when viewed in moderate quantity, but when seen in bulk, it possesses a bluish-green color. The water of the sea and of deep lakes is usually bluish-green. Some lake waters which are relatively pure, however, have a brownish hue on account of organic matter. Thus, the water of Loch Katrine, in Scotland, is nearly chemically pure, but it has a perceptible brownish tint due to traces of organic matter taken up from the peat of the surrounding country. Water is only slightly compressible, 1,000,000 volumes being reduced by 50 volumes when the atmospheric pressure is doubled. Water is a poor conductor of heat, as may be shown by placing a piece of lead above a lump of ice contained in a test-tube about three-fourths full of water, and then heating the water to boiling in the upper part of the tube. Pure water, like all other pure liquids, is a very poor conductor of electricity. At 760 mm. pressure, water exists as a liquid between 0° and 100° .

When water is heated or cooled at temperatures above 4° , it follows the general law, that bodies expand when heated and contract when cooled. When cooled from 4° to 0° , it expands; on being heated from 0° to 4° , it contracts, reaching its maximum density at 4° (really 3.98°). Water therefore expands on freezing, but other liquids, as a rule, contract. 11 volumes of ice melt into 10 volumes of water at 0° . The volume of water at 100° is 1.043 times that at 4° .

1 cc. of water at 4° weighs 1 g., which is the unit of density.¹ The abnormal behavior of water between 4° and 0° has a marked influence upon climate and hence upon life. If water followed the general law of liquids between 4° and 0° , our large bodies of fresh water would be converted into solid masses of ice during long, cold winters, which the warmth of summer would not be sufficient to melt.

The freezing point and boiling point of water are much higher than those of related compounds having molecular weights near that of water, as the following table shows:

<i>Name of Substance</i>	<i>Formula</i>	<i>Molecular Wt.</i>	<i>F. Pt.</i>	<i>B. Pt.</i>
Water	OH_2	18	0°	100°
Ammonia	NH_3	17	-78°	-33°
Methane	CH_4	16	-184°	-160°

¹ The absolute density of water at 4° is 0.999973, which is practically 1.

The amount of heat required to raise 1 g. of water 1° C. (from 15° – 16°) is called a **calorie**; therefore, when a gram of water cools one degree, a calorie is liberated. When large volumes of water cool down, much heat is liberated, which tempers the climate in the vicinity of the ocean. Moreover, water has a high **specific heat**, the specific heat being the number of calories required to raise a gram of a substance one degree. The specific heat of water is, therefore, 1, while that of practically all other known liquids and solids is less than 1.¹ Thus, the temperature changes of large masses of water are more gradual than those of the land. This means that a continental climate is not as even as that of an island.

It requires 79 calories to convert 1 g. of ice at 0° into liquid. The **heat of fusion of ice** is therefore said to be 79 thermal units. A mixture of water and ice, at equilibrium, has a temperature of 0° — the melting point or the freezing point of water. The change in temperature of a very small fraction of a degree will cause the ice to melt or the liquid to freeze. Under certain conditions water may be supercooled without the appearance of ice, but the introduction of a small amount of the latter induces freezing at once.

Under a pressure of 760 mm. water boils at 100° , *i.e.*, it gives off steam freely at constant temperature. It requires about 540 calories to convert 1 g. of water at 100° into steam at the same temperature. 540 is called the **heat of vaporization of water**. 1 liter of water gives about 1,600 liters of steam at 100° .

141. The Vapor Pressure Curves of Water; Equilibria. — Liquid water has a vapor pressure which increases with temperature, amounting to 760 mm. of mercury at 100° , its boiling point. At 374° water reaches its critical temperature. When cooled, water forms ice at 0° under a pressure of one atmosphere. Ice also has a measurable vapor pressure, which is 4.579 mm. of mercury at 0° . The vapor pressure is lowered by increase in pressure. *In the water system there are the following equilibria:*

- (1) Liquid water and its vapor: $\text{water} \rightleftharpoons \text{vapor}$.
- (2) Ice and vapor: $\text{ice} \rightleftharpoons \text{vapor}$.
- (3) Solid and liquid: $\text{ice} \rightleftharpoons \text{water}$.
- (4) Solid, liquid, and vapor, which exist together only at a fixed temperature — approximately 0° C.

In the four equilibria, only two variables are mentioned, namely, pressure and temperature. There can be no variation in composi-

¹ A certain strength of an aqueous solution of methyl alcohol is an exception.

tion, for each phase (solid, liquid, gas) is water under all conditions; that is, we have a *system of one component*.

The *pressure-temperature diagram for water* (Fig. 67) will aid in understanding the equilibria. The curve COt_c is the **steam line**, or **vaporization curve**, or **vapor pressure curve** for water. It represents the vapor pressure of water corresponding with a given temperature when liquid water and vapor are in contact and in equilibrium. The upper end of the vapor pressure curve is the

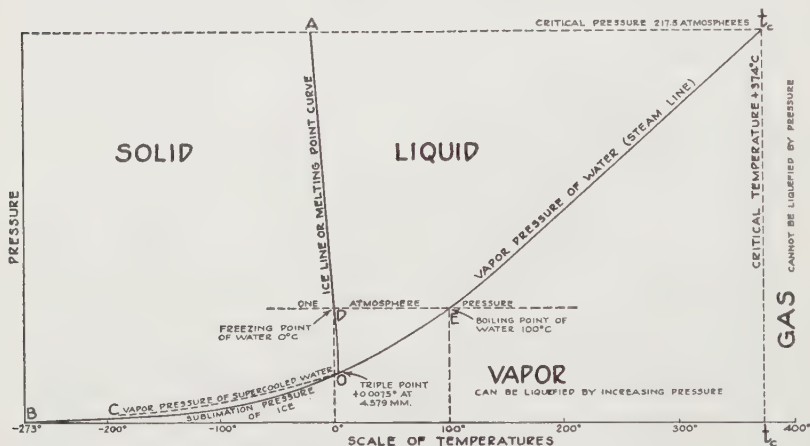


FIG. 67. Pressure-Temperature Diagram for Water.

critical point t_c , which is $+374^\circ \text{C}$.; the critical pressure is 217.5 atmospheres.

The temperature at which water ordinarily freezes is represented by point O . With care, water may be cooled below this temperature without the formation of ice (173); this fact is represented by a prolongation OC of the vapor pressure curve, and there is still perfectly definite relations of pressure to temperature. The curve OB represents the equilibrium curve for ice and vapor, and is known as the **sublimation curve**, or **hoar-frost line**. The point represented by B is assumed to be absolute zero. The water-vapor curve OC and the ice-vapor curve OB intersect at O .

The curve AO is known as the **ice line** or **fusion curve**. This curve slopes gently from left to right, which shows that the melting point of ice is lowered by increasing the pressure. *In vacuo* ice melts at about $+0.0075^\circ$.

The **triple point** *O* is the point at which ice and vapor are in equilibrium and water and vapor are in equilibrium, the vapor pressure being the same in both cases. Ice and water are also in equilibrium. The temperature and pressure corresponding to the triple point are respectively 4.579 mm. of mercury and $+0.0075^{\circ}$. This is the freezing point of water under its own vapor pressure of 4.579 mm., whereas the value 0°C. is the freezing point of water under an external pressure of one atmosphere.

Water, ice, and water vapor can exist in equilibrium only at the triple point; if either temperature or pressure be changed, one phase of the system will be eliminated in order to restore equilibrium.

142. Pressure of Aqueous Vapor. — Water, including ice and snow, constantly gives off vapor at all temperatures. Thus, when water is left in an open vessel in a room, it evaporates. The evaporation of liquids has already been explained (59). When a small quantity of water is introduced above the mercury in a barometer (Fig. 68), some of it forms a vapor, and the pressure of the vapor may be measured by observing the depression of the column of mercury. The hotter the water, the greater is the pressure of its vapor, as may be shown by pouring hot water into a jacket surrounding the top of the barometer. In the figure, the distance from *A* to *B* represents the pressure of the water vapor formed by introducing a drop or two of water above the mercury. Examine the vapor pressure curve of water from 0° to 100° (Fig. 82). A liquid boils when its vapor pressure becomes equal to the pressure of the atmosphere. Thus, water boils at 100° when the atmospheric pressure is normal (760 mm.). On the summits of mountains, where the pressures are lower, water and other liquids have lower boiling points. At Quito, for example, which is 2,914 meters above the level of the sea, the mean height of the barometric column is 523 mm.; therefore the boiling point of water is only 90.1° .

When an excess of water is introduced into a barometer, the vapor pressure soon reaches a maximum, which is constant at a definite temperature, say, 20° . *The maximum vapor pressure represents the vapor tension of the liquid.* For water at 20° , it is 17.4 mm. (see Appendix). In the case of water, the maximum

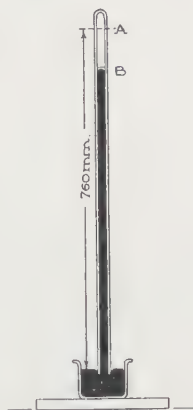


FIG. 68.

value of the vapor pressure at a given temperature is called the **aqueous tension**. The aqueous tension (pressure of the vapor) of water is 4.58 mm. at 0° , 31.55 at 30° , 148.79 at 60° , 760 at 100° , 10 atmospheres (10×760 mm.) at 180.3° , and 25 atmospheres at 224.7° .

143. **Water Vapor in Gases.** — When gases are collected over water, water vapor is always mixed with the gases (Dalton's law, 49). We have seen that in reducing the volume of a gas to the dry condition, a correction must be made for the pressure due to water vapor.

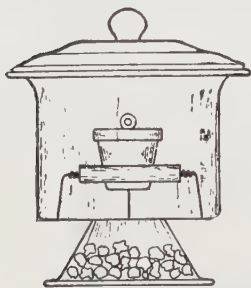


FIG. 69.

Likewise, water gives up vapor to the atmosphere. The air is, on the average, less than two-thirds saturated with water vapor. However, the amount of water vapor in the air varies greatly in different localities and from time to time. A space is said to be saturated with water vapor when water at a certain temperature has given the maximum amount of vapor to the space, permitted by its aqueous tension.

All bodies and substances when exposed to the atmosphere have more or less water condensed upon their surfaces. In order to get rid of traces of water, the body or substance is heated, and then allowed to cool in a desiccator (Fig. 69). A desiccator is a glass vessel with an air-tight cover; it contains some desiccating agent, such as calcium chloride or concentrated sulfuric acid.

144. **Equilibrium.** — The molecular relation of liquid and vapor was briefly discussed in connection with the kinetic theory (59). To use another illustration, when an excess of water is introduced into the Torricellian vacuum of a barometer, vapor forms, and kinetic equilibrium is soon established. When the water is first introduced, there are no molecules of water vapor above the liquid. The number of molecules of water passing into the state of vapor is constant per unit of time, being determined by the aqueous tension of water at the given temperature. The number plunging back into the liquid is zero at first, but gradually increases until the number returning to the liquid state is just equal to the number leaving. When this condition is reached, it is called *kinetic equilibrium*, for it is dynamic and not static.

The following are the *characteristics of a state of equilibrium*:

(1) *There are always two opposing tendencies or actions which exactly counteract each other at equilibrium.*

Thus, in the case of water at equilibrium, the vapor tension of the liquid, which is determined by the number of molecules of water leaving the liquid in a unit of time, is just equal to the vapor pressure of the vapor, which is represented by the number of molecules plunging back into the liquid in a unit of time. The opposing, balanced actions may be expressed thus:

Water (liquid) \rightleftharpoons Water (vapor).

(2) *At equilibrium, both tendencies or actions are still in full operation.*

(3) *A slight change in the conditions produces a corresponding change in the state of the system.* In other words, if any change is made in the system, the equilibrium is upset or thrown out of balance. To illustrate, if the temperature of the water be raised, more will evaporate until a new state of equilibrium is established at the new temperature; if the temperature be lowered, more water will condense.

145. **Water as a Solvent.** — Water is the substance most generally used as a solvent. Some solids, such as sugar and salt, are readily soluble in water; others, such as sea-sand (silica) and silver chloride, are so very slightly soluble that they are called “insoluble” substances. Liquids, such as acetic acid and alcohol, dissolve in water in all proportions; while other liquids, such as ether, are sparingly soluble. Such gases as ammonia and hydrogen chloride are extremely soluble in water, carbon dioxide is sparingly soluble, and oxygen and hydrogen only slightly soluble. There is no known substance which is entirely insoluble in water. Even finely divided glass, quartz, gold, and platinum dissolve in minute amounts.

146. **Natural Waters.** — No water found in nature is perfectly pure. Rain is virtually distilled water; but when it falls, various gases and solids, such as nitrogen, oxygen, carbon dioxide, and ammonium nitrate, are dissolved; also, insoluble matter, such as particles of dust, pollen grains, and bacteria is carried down. Moreover, when water percolates through the soil, it has a solvent action upon various substances, such as limestone and calcium sulfate. The water finding its way into rivers, lakes, and ocean contains not only matter in solution, but suspended matter. Even clear spring water and rain water are not pure. The impurities found in water can be divided into two classes:

(a) *Mechanically suspended impurities;*

(b) *Soluble impurities.*

147. Mechanically Suspended Impurities. — Suspended impurities may be removed from water (1) by filtration, or (2) by allowing the suspended matter to settle.

On a large scale, the process of filtration is carried out by means of beds of sand and gravel. Most of the suspended matter, including bacteria, is removed (Fig. 70).

The household filters, which were formerly used quite extensively, are not very efficient in removing disease-producing organisms.

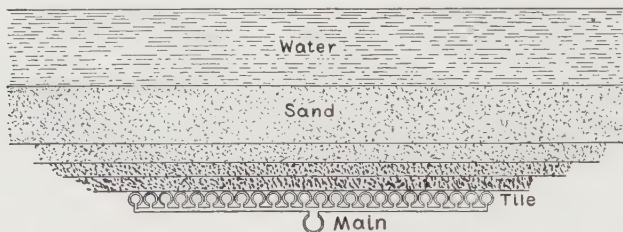
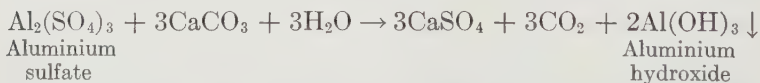


FIG. 70.

Boiling the water for 10 or 15 minutes is much more effective. If necessary, the water can be boiled a second time.

Water is also run into large settling tanks, and small amounts of alum, aluminium sulfate, or other substances are added; a slimy precipitate is formed, and suspended matter, including micro-organisms, attaches itself to the gelatinous precipitate and is finally carried to the bottom of the tank. With water containing the requisite amount of alkalinity, a flocculent precipitate of aluminium hydroxide is formed:



Even after filtration or the coagulation treatment, water still contains some bacteria. To make it safe for drinking, small quantities of germicides are added, such as chlorine or bleaching powder. Water is also treated with ozone and with ultra-violet light. Water may also be purified by distillation. The Liebig still is quite generally employed in laboratories for distilling liquids (Fig. 71).

148. Soluble Impurities. — Waters containing soluble impurities may be divided into a number of classes, some of which are:

(1) **Soft Waters.** Soft waters are comparatively free from mineral salts. They are found in districts where quartz sand and sandstone occur.

(2) **Hard Waters.** These waters contain in solution certain mineral salts, especially the salts of calcium and of magnesium. They are found in limestone and dolomite districts; also where gypsum occurs. Hard waters are objectionable, for they consume large quantities of soap and often form boiler-scale, which means that a larger amount of fuel is required to generate steam. It has been estimated that a layer of scale a quarter of an inch thick on the boiler tubes requires 50 per cent more fuel in generating steam. It is difficult to remove boiler-scale; and now and then the thick scale cracks, thus exposing very hot iron to steam, causing an explosion.

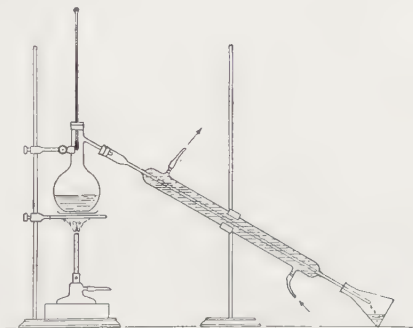
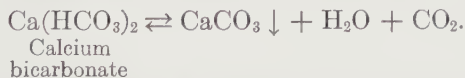


FIG. 71.

Hard waters are divided into two classes:

(a) *Temporarily hard waters* contain bicarbonates of calcium or magnesium. Such waters are found in limestone and dolomite districts. Waters containing in solution the bicarbonates of calcium and of magnesium may have the "hardness" removed by boiling, the metals being thrown out of solution in the form of carbonates:



CO_2 escapes and CaCO_3 is thrown out of solution and may be filtered off. This may be shown by the following experiment:

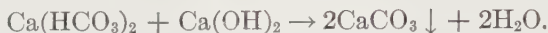
CO_2 is bubbled through a solution of calcium hydroxide (lime-water, $\text{Ca}(\text{OH})_2$) until a precipitate forms:



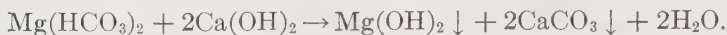
Then the current of CO_2 is continued until the CaCO_3 goes into solution, forming calcium bicarbonate, $\text{Ca}(\text{HCO}_3)_2$. When the solution is boiled, CaCO_3 is reformed. The action is reversible:



Temporarily hard water also may be softened by the addition of calcium hydroxide:



In case magnesium bicarbonate is in solution in water, sufficient lime must be added to convert the magnesium carbonate into magnesium hydroxide:



The use of lime in the softening of water was introduced by Thomas Clark.

(b) *Permanently hard waters.* Such waters contain in solution salts (usually sulfates) of such metals as calcium and magnesium. When water flows through beds of gypsum, calcium sulfate is dissolved. These waters may be softened by adding sodium carbonate ("washing soda"):



Calcium carbonate is precipitated, and sodium sulfate remains in solution; but salts of sodium and potassium do not render water hard. This method was developed by another chemist, J. H. Porter. The Porter and Clark processes may be combined, the insoluble CaCO_3 and $\text{Mg}(\text{OH})_2$ being filtered off.

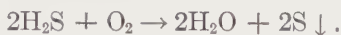
Mineral waters contain various components, which are usually not present in appreciable quantities in ordinary water. Some of the kinds of **mineral waters** are as follows:

(1) **Effervescent Waters.** These waters are rich in carbonic acid. When CO_2 escapes, the water is said to effervesce. The Seltzer and Apollinaris waters are among the best known. These waters are often called carbonated waters. They contain small quantities of alkali salts.

(2) **Alkaline Waters.** These waters contain very appreciable quantities of such salts as sodium bicarbonate, sodium chloride, and sodium sulfate. *Vichy water* is used in the treatment of certain diseases, such as acidosis: the alkali salts neutralize the acids of the body. The temperature of the springs at Vichy is about 45°C .

(3) **Chalybeate Waters** contain salts of iron, especially ferrous bicarbonate. They are used in medicine. When exposed to the air, ferruginous waters give a brownish-red precipitate of ferric hydroxide.

(4) **Sulfur or Hepatic Waters** contain hydrogen sulfide (H_2S) and other sulfur compounds. They possess a disagreeable odor, and are used for skin disorders. One of the best known sulfur waters is that of White Sulfur Springs. On exposure to air, sulfur waters deposit sulfur:



(5) **Bitter or Saline Waters.** These contain various salts. Epsom water contains magnesium sulfate; Marienbad water, sodium sulfate; and Hunyadi water, sodium and magnesium sulfates.

149. **Water and Health.** — A pure water supply is very essential for the health of a city or community. In recent years so much attention has been given to the subject that typhoid fever is almost negligible in large cities. Water which is apparently pure may contain pathogenic organisms — germs of typhoid, cholera, or anthrax. To insure pure water for drinking, it should be examined frequently by the biologist and the chemist. The object of a bacteriological examination is to detect the numbers and kinds of organisms present. The detection of disease-producing organisms is a matter of considerable difficulty. Such an examination of water is chiefly valuable as a test of the efficacy of the processes used in its purification.

Chemical analysis of a water is more rapid than a bacteriological examination, and while it leaves much to be desired, it affords valuable indications. Thus, if a water contains much nitrogen either in the form of albumin or albuminous matter, or as decomposition and oxidation products — ammonia, nitrites, or nitrates — it shows pollution with animal matter, likely sewage. A high content of chlorine as sodium chloride usually indicates sewage pollution. Wherever animal matter or sewage is present, disease-producing bacteria may be present also.

150. **Chemical Properties of Water.** — (1) Water is a stable compound. At high temperatures, however, it dissociates into its elements:



At $2,650^\circ$ and 1 atmosphere of pressure, water is 11 per cent dissociated; at $2,000^\circ$, 1.8 per cent (less than 2 molecules of steam in every hundred are dissociated). The dissociation increases with increased temperature and under lower pressures. The

breaking down of water into its constituents and the reuniting of the latter at lower temperatures to form water is an illustration of *dissociation*. Note that the breaking down of potassium chlorate (KClO_3), when heated, is decomposition, for the action is not reversible (97).

(2) Water interacts with the more active metals to form hydrogen (122).

(3) Water interacts with anhydrides to form acids, and with basic (metallic) oxides to form bases (99).

(4) Water interacts with certain substances, especially salts, to form *hydrates*.

151. **The Composition of Water.** — The composition of water may be studied (I) gravimetrically, and (II) volumetrically.

(I) *Composition by weight.*

(a) Method used by Berzelius and Dulong.

The method of determining the composition of water by weight was first carried out by Berzelius and Dulong in 1819.

In 1842 Dumas and Stas repeated the work of Berzelius and Dulong with a much higher degree of accuracy. Omitting details, suffice it to say that Dumas passed pure, dry hydrogen over a known weight of hot cupric oxide (CuO), and weighed the water which was formed. The loss in weight of the CuO was the weight of oxygen uniting with hydrogen, and the difference between the weight of the water and the weight of the oxygen was the weight of the hydrogen. As the result of nineteen experiments it was

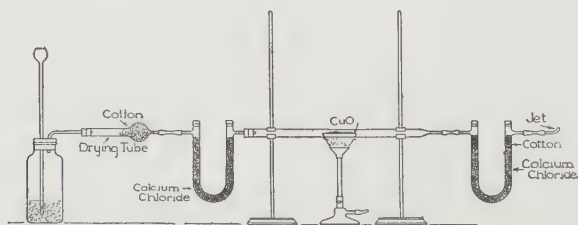


FIG. 72.

found that 840.161 g. of oxygen yielded 945.439 g. of water. This showed that 105.278 g. of hydrogen were required to reduce the CuO ; or, 1 part by weight of hydrogen combined with 7.98 parts of oxygen, or 2 parts of hydrogen with 15.96 of oxygen. The chemical change is represented thus:



The synthesis of water by the Dumas method may be readily accomplished by passing dry hydrogen over about 5 g. of previously heated CuO contained in a porcelain boat, as shown in Fig. 72. The water is absorbed in calcium chloride. It should be added that Dumas employed a more complicated apparatus.

(b) Dumas' experimental work was the best until 1888, when Cooke and Richards carried out experiments leading to the ratio 2 : 15.90, or $2 \times 1.0063 : 16$.

(c) Edward Morley, an American chemist, synthesized water (1895) from pure hydrogen and oxygen, all of which were carefully weighed. He obtained the ratio 2.016 : 16, or 2 : 15.879, which is considered to be a very trustworthy result.

Morley was the first experimenter actually to weigh the three substances concerned, whereas all his predecessors obtained one or another of these substances by difference. The form of apparatus employed by him is shown in Fig. 73. Hydrogen was delivered to the apparatus at *a* and oxygen at *a'*. The two gases passed through the tubes *c*, *c*, and their chemical combination was brought about by electric sparks. The resulting steam was condensed, the water frozen, and any uncombined gases removed and their quantity determined. The tubes *b*, *b* contained phosphorus pentoxide, P_2O_5 , for the removal of moisture from the gases. The vessel was weighed, the gain in weight representing the water formed. The hydrogen was absorbed in palladium and weighed, while the oxygen was weighed in a large globe. Morley used every known precaution.

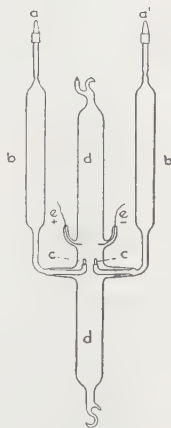


FIG. 73.

(II) *Composition by volume.*

(a) Cavendish (1781) exploded 2 volumes of hydrogen mixed with 1 volume of oxygen and obtained water in the liquid state.

(b) Gay-Lussac and Humboldt (1805) obtained the ratio 2 : 1.

(c) Morley (1895) obtained the ratio 2.00269 volumes of hydrogen to 1 volume of oxygen.

When 2 volumes of hydrogen mixed with 1 volume of oxygen ("electrolytic gas") are exploded in a simple eudiometer by means of an electric spark, the steam condenses and the gases vanish. In case different proportions are mixed, either hydrogen or oxygen will be left over.

152. **The Volumetric Synthesis of Steam; Gay-Lussac's Law.** — If the experiment just described be performed in a eudiometer surrounded by a steam jacket, the water is obtained as steam, and its volume thus found. The experiment is carried out in an

apparatus as shown in Fig. 74. Hydrogen and oxygen (electrolytic gas) are generated by the electrolysis of water containing in solution a small quantity of sodium hydroxide. The carefully dried gases, say, 20 cc. of hydrogen and 10 cc. of oxygen, are passed into the eudiometer, and are confined above mercury. An electric spark produced by an induction coil is passed through the mixture, which causes an explosion, with the production of water vapor. The volume of gas decreases. The temperature remains constant throughout (100°), and the tube containing the steam is so adjusted that its volume is read off under the same pressure as that of the combining gases. Approximately 20 cc. of steam should be obtained. The volume of steam is, therefore, equal to the volume of the hydrogen and to double that of the oxygen:

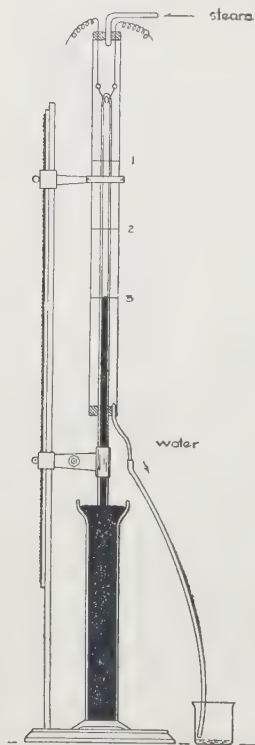
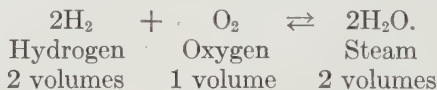


FIG. 74.



We see that when the gases unite to form a gaseous product, all the volumes of the gases are simply related to one another (2 : 1 : 2).

This experiment is a good illustration of Gay-Lussac's Law of Combining Vol-

umes, which was enunciated in 1808. The law may be stated thus:

When gases combine chemically, they do so in volumes which bear a simple ratio to one another, and to the volume of the product, if gaseous.

It is understood, of course, that the volumes of all the gases are measured under the same conditions of pressure and temperature.

153. **Hydrates.** — Many substances on crystallizing from aqueous solutions unite with water to form compounds known as hydrates: *e.g.*, gypsum, or the hydrate calcium sulfate; blue vitriol, or the hydrate copper sulfate. When a hydrate is heated, it gives up water. This may be shown by heating a crystal of

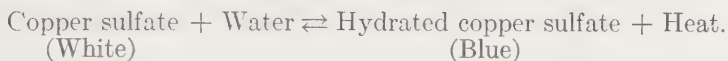


HENRY CAVENDISH (1731-1810).



JOSEPH LOUIS GAY-LUSSAC (1778-1850)

gypsum or of blue vitriol in a clean, dry test-tube. Water deposits upon the colder part of the tube, and a powder — the anhydrous salt — is left in the test-tube. Anhydrous copper sulfate is whitish. If a little of the powder be sprinkled on a piece of filter paper and then moistened with water, it turns blue and heat is liberated, on account of the formation of the hydrated salt:



The action is reversible.

Are hydrates definite chemical compounds? If so, their composition should conform to the law of constant proportions and there should be a definite chemical formula for every hydrate. Chemical analysis shows that hydrates have definite or constant composition; they are, therefore, chemical compounds.

Example. — 2.105 g. of gypsum were heated in a crucible to constant weight, which was found to be 1.667 g. Find the formula of the hydrate, assuming the formula of the anhydrous sulfate to be CaSO_4 . [Atomic weights: $\text{Ca} = 40$, $\text{S} = 32$, $\text{O} = 16$.]

Wt. of hydrate..... = 2.105 g.

Wt. of anhydrous salt..... = 1.667 g.

Wt. of water..... = 0.438 g.

The gram-molecular wt. of $\text{CaSO}_4 = 40 + 32 + (4 \times 16) = 136$ g.

The gram-molecular wt. of $\text{H}_2\text{O} = 18.016$ g.

RATIO OF MOLECULES

$$1.667 \div 136 = .012$$

$$0.438 \div 18.016 = .024$$

$.012 : .024 = 1 : 2$; therefore, the formula is $\text{CaSO}_4 : 2(\text{H}_2\text{O})$, which is usually written $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. This formula shows that gypsum is a dihydrate, *i.e.*, it has two molecules of water of hydration, which is sometimes called “water of crystallization.” There are some objections to the latter term, however, and it is not as much used as formerly.

Other common hydrates are as follows:

Copper sulfate (blue vitriol).....	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
Barium chloride.....	$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$
Epsom salt.....	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$
Washing soda.....	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$
Glauber's salt.....	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$
Sodium phosphate.....	$\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$

Many salts crystallize from water without combining with it, such as:

Sodium chloride.....	NaCl
Potassium chlorate.....	KClO ₃
Potassium dichromate.....	K ₂ Cr ₂ O ₇

Hydrates are unstable and have therefore a tendency to lose water, particularly when they are heated, or when exposed to low pressures. Solutions prepared by dissolving the hydrate and the anhydrous salt are identical, provided they are of equal concentration and density.

154. **Efflorescence.** — We have just seen that many salts form definite compounds with water, and are therefore called hydrates. Why do certain hydrates, such as washing soda and Glauber's salt, when exposed to the air, lose water and crumble to powder, while others, such as gypsum and blue vitriol, do not show this tendency? In other words, why do certain hydrates *effloresce*, while others do not? The dissociation (efflorescence) of a hydrate depends upon its stability and the conditions under which it is kept. Thus, a hydrate dissociates (loses water) faster at higher temperatures than at lower temperatures, and under lower pressures than under higher.

If a crystal of sodium phosphate or of Glauber's salt be passed above the mercury in a barometer tube, the salt gives off vapor which forces down the column of mercury to a certain extent; that is to say, there is a certain pressure of water vapor, which may be measured by noting the depression of the column of mercury. The vapor pressure of a hydrate is definite under given conditions, and vapor pressure curves showing the dissociation of hydrates at different temperatures are different for different substances.

Hydrates which, when exposed to the air in open vessels, have a vapor pressure greater than the partial pressure of the water vapor in the air, effloresce. Thus, washing soda loses water when exposed to the air. Gypsum and blue vitriol, on the other hand, have vapor pressures less than that of the partial pressure of the water vapor in the air, consequently they do not give up their water of hydration. Thus, the vapor pressure of blue vitriol at 25° is only 7.4 mm.; while the partial pressure of the water vapor of the atmosphere, which is usually less than two-thirds saturated at the given temperature, would be about 15 mm.

Hydrates, due to loss of water, have a vapor tension, and by

measurement of the vapor tension of a hydrate, *e.g.*, copper sulfate, information is obtained concerning the existence of other hydrates.

By experiment it has been demonstrated that there are several hydrated copper sulfates. The diagram (Fig. 75) illustrates the system, copper sulfate-water. At 50°, the pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) has a vapor tension of 47 mm., but when the proportion of water falls to $\text{CaSO}_4 \cdot 3\text{H}_2\text{O}$, the vapor tension suddenly

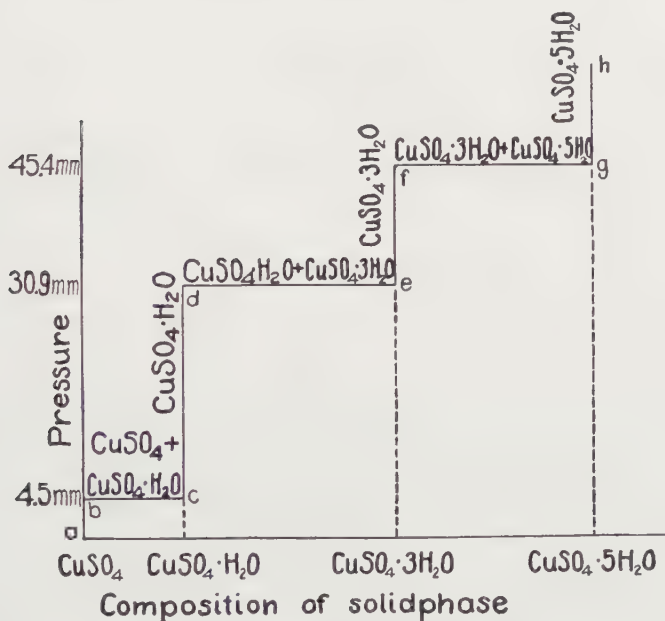


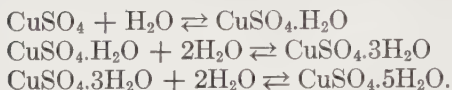
FIG. 75. The System, Copper Sulfate-Water.

drops to 30 mm. The salt then continues to lose water, without change in aqueous tension, until the monohydrate $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ is formed, and at this point the vapor pressure drops to 4.5 mm., and there is no further change in pressure until all the water has been removed. The anhydrous salt, of course, has no vapor tension.

On the other hand, if anhydrous copper sulfate be placed in a vessel and water vapor introduced continuously, the pressure will rise continuously along *ab* from zero pressure to 4.5 mm. before any water is taken up by the salt, since up to *b* the pressure of water vapor is less than the dissociation pressure of $\text{CuSO}_4 \cdot \text{H}_2\text{O}$.

At *b* $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ begins to form, and there is no increase in pressure until the formation of the monohydrate is complete. At *c* the pressure again rises until it reaches 30 mm., whereupon the trihydrate $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$ begins to form. When the formation of the trihydrate is complete, the pressure rises once more, and when it reaches 47 mm. the pentahydrate begins to form.

The reversible actions with the progress of hydration are:

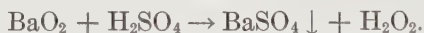


HYDROGEN PEROXIDE

155. Preparation. — Hydrogen peroxide was first prepared in 1818 by Thénard, who treated barium dioxide with dilute hydrochloric acid:



It is usually prepared by treating BaO_2 with dilute sulfuric acid:



The dilute aqueous solution obtained is concentrated (*a*) by allowing it to stand over concentrated sulfuric acid *in vacuo*, (*b*) by distilling under diminished pressure, or (*c*) by carefully evaporating off the water in open vessels. By distilling *in vacuo*, Merck prepares "superoxol," which contains 30 per cent of H_2O_2 .

Hydrogen peroxide may also be prepared by treating Na_2O_2 with dilute acids, and by passing CO_2 through BaO_2 suspended in water.

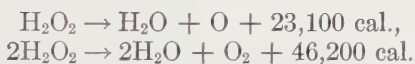
Hydrogen peroxide is formed in many cases during oxidation. Thus, when a jet of burning hydrogen is allowed to impinge upon cold water or ice, a small quantity of hydrogen peroxide may be found in the water. It is also formed by the action of bright sunlight on water containing oxygen in solution.

156. Test for Hydrogen Peroxide. — When a solution of hydrogen peroxide is acidulated and a drop or two of a solution of potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) is added, a beautiful coloration is produced. The blue substance is an unstable perchromic acid. As this substance is more soluble in ether than in water, the test is rendered more delicate by shaking the liquid with ether. On standing the latter rises to the top, carrying with it most of the perchromic acid.

Hydrogen peroxide also liberates iodine from potassium iodide, which gives a blue color with starch (see Ozone).

157. Physical Properties. — Anhydrous hydrogen peroxide, which was not obtained until 1894, is a clear, syrupy liquid, colorless in small amounts, but bluish when viewed in bulk (see Water). Its odor suggests that of nitric acid. Its specific gravity is 1.4584 at 0°. The liquid boils at 69.2° under a pressure of 26 mm., or at 84–85° under 68 mm. When cooled, it forms anhydrous crystals, melting at –2°. It has a metallic taste when diluted, and blisters the skin. Determination of the freezing points of solutions of hydrogen peroxide shows that its formula is H_2O_2 (177).

158. Chemical Properties. — Many of the chemical properties of hydrogen peroxide are similar to those of ozone (116). Both are endothermic substances and are therefore unstable, the molecule of each having a tendency to part with an atom of oxygen:



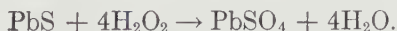
The decomposition of H_2O_2 is accompanied by the liberation of a large quantity of heat. When the dilute aqueous solution is free from impurities, it keeps fairly well. Many substances accelerate its decomposition. Thus, manganese dioxide, finely divided metals, free alkalies, and even any rough surfaces on the inside of the containers act as catalysts. Traces of acetanilide or of sulfuric acid serve as “negative catalysts.” Free acids must not be used, however, to stabilize it for medicinal use.

Oxygen is readily liberated by introducing some manganese dioxide into about 10 cc. of a 3 per cent solution of hydrogen peroxide contained in a test-tube.

When a 3 per cent commercial solution of hydrogen peroxide breaks down, 10 times its volume of oxygen is liberated; hence it is called a “10 volume solution.”

Hydrogen peroxide is an oxidizing agent, for it readily breaks down, yielding oxygen and water, together with a large quantity of energy.

When lead sulfide, which is black, is treated with a solution of hydrogen peroxide, it is oxidized to lead sulfate, which is white:



This reaction is utilized in restoring the color to old oil paintings.

The white-lead pigment used by the artist is gradually converted into lead sulfide, due to the action of the hydrogen sulfide in the air.

Hydrogen peroxide liberates iodine from hydrogen iodide:



The oxidizing action of hydrogen peroxide is utilized in bleaching delicate materials, such as silk, wool, feathers, hair, etc., which would be injured by chlorine. Thus, when hair is treated with hydrogen peroxide, it is bleached to a golden-yellow color. As an oxidizing agent, it is also used as an antiseptic: *e.g.*, as a gargle. When H_2O_2 acts as an oxidizing agent, water, a harmless by-product, is formed.

Hydrogen peroxide reduces the oxides of certain metals, such as silver and gold:

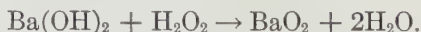


It is of interest to note that in this case we have an active oxidizing agent acting as a reducing agent. This is no doubt due to the fact that the oxides of the noble metals are unstable compounds; that is, the oxygen is in feeble union with the metal. Hydrogen peroxide holds one atom of oxygen in feeble combination, so Ag_2O and H_2O_2 mutually reduce each other, an atom from each molecule combining to form a molecule of oxygen (O_2).

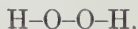
It also is an interesting fact that hydrogen peroxide and potassium permanganate — both oxidizing agents — reduce one another, oxygen being liberated:



Hydrogen peroxide is a feeble acid. The **peroxides**, such as Na_2O_2 and BaO_2 , are regarded as salts of hydrogen peroxide. When barium hydroxide is treated with an aqueous solution of hydrogen peroxide, hydrated barium peroxide ($\text{BaO}_2 \cdot 8\text{H}_2\text{O}$) is obtained as a crystalline precipitate:



When peroxides are treated with dilute acids, hydrogen peroxide is formed (155). The structural formula for hydrogen peroxide is usually written thus:



Peroxides appear to contain the group



159. **Uses of Hydrogen Peroxide.** — Hydrogen peroxide is used for bleaching silk, wool, hair, feathers, ivory, etc.; for restoring color to old paintings; in medicine as an antiseptic and cleansing agent; and in the laboratory as an oxidizing agent.

While hydrogen peroxide is a germicide, its action as such has been overestimated by the public. It is particularly serviceable for expelling pus, for loosening dried bloody bandages, and when a mild oxidizing agent is needed.

EXERCISES

1. Write chemical equations showing the formation of water.
2. State the physical properties of water. Why is it that during a long and extremely cold winter the water of our deep ponds and lakes does not freeze *en masse*? Show that large bodies of water make an island climate milder than that of a continent in the same latitude.
3. Define the following: calorie, specific heat, heat of fusion, heat of vaporization, and boiling point.
4. Define and illustrate what is meant by aqueous tension. When is a given space said to be saturated with water vapor?
5. State the three characteristics of a state of equilibrium.
6. Classify natural waters, and explain, including equations, how hard waters may be softened.
7. How may waters be purified?
8. State the comparative values of a chemical analysis and a bacteriological examination of a water.
9. Write equations to show the chemical properties of water.
10. Outline methods for (1) the gravimetric composition of water, and (2) for the volumetric synthesis of steam. Show how the volumetric synthesis of steam illustrates Gay-Lussac's law.
11. 150 cc. of hydrogen are mixed with 60 cc. of oxygen, and the mixture exploded by means of an electric spark. Assuming that all the gases are measured at S.T.P., what volume, if any, of gas will remain and how you would determine what it is.
12. What is the difference between hydrates and hydroxides? What evidence have we that hydrates are definite chemical compounds? Explain fully why certain hydrates effloresce when exposed in open vessels, while others do not.
13. A salt hydrate was found to contain 15.65 per cent of sodium, 16.54 of arsenic, 21.17 of sulfur, 3.54 of oxygen, and 43.10 per cent of water. Find its simplest formula.
14. Show that when a small quantity of water or a crystal of a hydrate is introduced into a barometer above mercury, an equilibrium (kinetic) is soon established.

15. (a) Reduce 500 cc. of hydrogen, measured over water at 21° and 759 mm., to the dry condition and to S.T.P. (b) What weights of zinc and of sulfuric acid containing 15 per cent of H_2SO_4 would be required to generate the volume of hydrogen obtained in (a)?

16. Starting with barium monoxide, show how you would obtain barium peroxide, and then write three different equations showing how hydrogen peroxide may be prepared by the use of barium peroxide.

17. How may a solution of hydrogen peroxide be freed from water?

18. Point out all the resemblances you can between hydrogen peroxide and ozone. How would you identify each substance?

19. Give fully, including equations, the chemical properties of hydrogen peroxide, paying particular attention to its oxidizing action. Explain why it reduces certain oxides.

20. Discuss the action of catalysts upon hydrogen peroxide.

21. Can you offer any reason as to why hydrogen peroxide is more unstable than water?

22. Why are such compounds as BaO_2 and Na_2O_2 (peroxides) regarded as salts of hydrogen peroxide?

23. Hydrogen peroxide contains 5.93 per cent by weight of hydrogen and 94.07 per cent of oxygen. Deduce its simplest formula. Why is not this formula taken as the molecular formula?

24. Water contains 11.11 per cent by weight of hydrogen. Find the combining weight of hydrogen. Has hydrogen the same combining weight in hydrogen peroxide?

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CHAPTER IX

SOLUTION

160. Definition of Solution. — We have seen that water has a powerful solvent action. In general, it is a better solvent for inorganic than for organic substances. Ether, the alcohols, carbon disulfide, benzene, carbon tetrachloride, etc., are excellent solvents for many substances and bodies which are practically insoluble in water. Thus, ether is a good solvent for oils and fats, the alcohols for resins, and carbon disulfide for phosphorus and sulfur.

We have also seen (5) that a solution is homogeneous, and, like an ordinary mixture, its composition is variable. A solution is transparent, but it may be colored. Thus, if we dissolve a small crystal of potassium permanganate in several liters of water, a highly colored liquid is obtained, which passes through a filter without change, and is homogeneous.

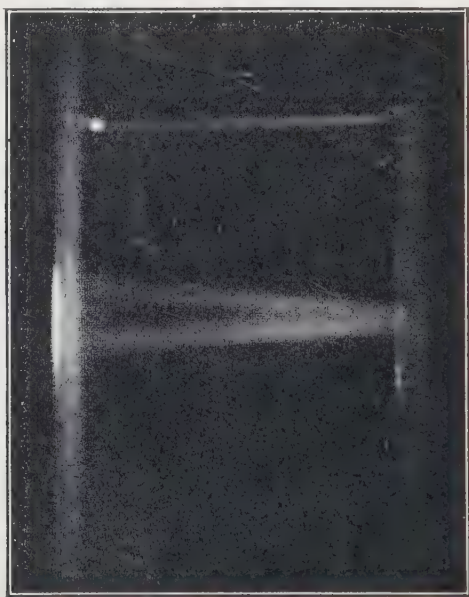
A solution is, therefore, an optically homogeneous mixture of two or more substances, the composition of which can be varied continuously between certain limits. There is absence of settling in solutions, and it is known that the dissolved matter is in an extremely fine state of subdivision — so fine that it passes through filters.

Again, if a small quantity of resin be shaken with alcohol, it dissolves, forming a homogeneous, colorless liquid. Both the potassium permanganate and the resin may be recovered by evaporating the solutions to dryness. The total solids in water can be determined readily by evaporating to dryness 100 g. of water and then weighing the residue.

Exceedingly minute quantities of certain substances have great coloring power. For example, one working with fluorescein dyes may have flecks enough fall into his hair to impart a powerfully fluorescent yellow-green color to the water of a large swimming-pool.

161. Colloidal Suspensions and Emulsions. — We have seen that matter may be in solution in water, or it may be merely in suspension. The coarser particles constituting a suspension settle sooner or later and may be removed by filtration. It is

possible, however, to prepare liquids that appear homogeneous to the eye and pass through ordinary filters without leaving a residue, but when a powerful beam of light in a darkened room is brought to a focus in the liquid lying under a microscope, the presence of suspended particles in the liquid is revealed (Fig. 76). Matter



Courtesy, P. Blakiston's Sons and Co.

FIG. 76. The Tyndall Phenomenon. (From "Hand-book of Colloid Chemistry" by Ostwald-Fischer.)

When a powerful beam of light in a darkened room is passed through a colloidal solution, the presence of small particles is revealed, the visibility of the beam being due to the scattering effect of the minute particles.

in this state of subdivision is said to be in **colloidal suspension** or **colloidal solution**. True solutions, as a rule, remain perfectly dark when a beam of light is passed through them.

A colloidal solution (suspension) of silver chloride may be prepared as follows:

About 0.25 g. of gelatin is dissolved by warming it with 25 cc. of distilled water contained in a test-tube. The liquid is cooled, two drops of concentrated hydrochloric acid added, and then the test-tube is shaken. An excess of a solution of silver nitrate is now added and the tube allowed to

stand a little while. No precipitate of silver chloride should be obtained. This may be contrasted with the addition of hydrochloric acid to a solution of silver nitrate.

An **emulsion** consists of droplets of one liquid suspended in another: *e.g.*, milk consists of globules of butter-fat floating in a nearly transparent liquid. Cod-liver oil is an emulsion of oil in water. Gelatin with water forms a typical emulsoid solution.

162. The Term Solution a Broad One. — Solutions are not restricted to any particular state of matter. Most frequently the word solution applies to solutions of solids in liquids; it also applies to liquids and gases in liquids, to gases in gases, and to the three states of matter in solids. Thus, hydrogen is absorbed by palladium and certain other metals (123), and solid solutions (alloys) of antimony and bismuth are well known.

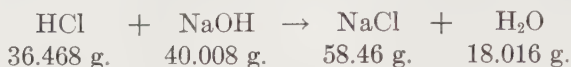
163. Definition of Terms. — The **solvent** is the substance which forms the main portion of the solution. The **solute** is the substance which is dissolved. Thus, sugar is the solute in a solution of sugar in water.

The weight of the solute in a unit volume of the solution is known as its **concentration**. The volume may be 1 cc. or 1 liter. We often say that so many grams of a substance dissolve in 100 g. of the solvent at a given temperature. Thus, 35.86 g. of NaCl may be held in 100 g. of water at 18°. This is a saturated solution of sodium chloride at 18°.

When chemical units of weight are employed, the concentration of solutions may be expressed either in terms of molecules or chemical equivalents; hence we have *molar solutions* and *normal solutions*.

164. Molar Solutions. — *A molar solution contains 1 mol (gram-molecular weight) of the solute per liter of solution.* Thus, a molar solution of NaCl can be prepared by dissolving 58.46 g. of pure salt in water, and then diluting to a liter. A molar solution of the hydrate Epsom salt ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) would contain $24.3 + 32 + (4 \times 16) + (7 \times 18.016)$ g. = 246.412 g. per liter.

165. Normal Solutions. — *A normal solution contains one gram-equivalent of the active substance in a liter.* Equal volumes of normal solutions are chemically equivalent to each other: *e.g.*, 1 liter of normal hydrochloric acid (36.468 g. of HCl per liter) will exactly neutralize 1 liter of normal sodium hydroxide (40.008 g. of NaOH):

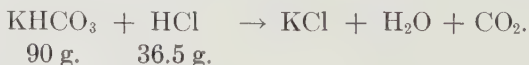


A normal solution of an acid contains 1 g. (to be exact, 1.008 g.) of active, or replaceable, hydrogen per liter. In other words, if a liter of a normal acid were treated with an excess of a metal, say, magnesium or zinc, 1 g. of hydrogen would be liberated from the acid. Thus, 36.5 g. of HCl contain 1 g. of hydrogen, all of which may be liberated; therefore 36.5 g. of HCl (one formula-weight, or equivalent weight) are required to prepare a liter of normal acid. The molecular weight of H_2SO_4 is 98; but 98 g. of the compound contain 2 g. of hydrogen, so to prepare a liter of normal acid 49 g of H_2SO_4 are required.

A molecule of acetic acid, $\text{H}(\text{C}_2\text{H}_3\text{O}_2)$, contains only one atom of hydrogen replaceable by a metal; therefore, the normal solution of the acid is of the same concentration as the molar, both requiring 60 g. of $\text{H}(\text{C}_2\text{H}_3\text{O}_2)$ per liter of solution.

A normal solution of a base contains 17 g. (to be exact, 17.008 g.) of available hydroxyl (OH) per liter. Thus, 40 g. of NaOH or 56 g. of KOH are required to prepare a liter of a normal solution. Theoretically, 37 g. of $\text{Ca}(\text{OH})_2$ would be required: $[40 + (2 \times 17)] \div 2 = 74 \div 2 = 37$; for a mol of calcium hydroxide contains 34 g. of OH. Such a solution could not be prepared, however, for $\text{Ca}(\text{OH})_2$ is sparingly soluble in water.

In general, a normal solution of a salt may be prepared by dividing the molar weight of the salt by the total valence of the metallic radical: e.g., a normal solution of NaCl contains 58.5 g. of the salt per liter, while one of CaCl_2 contains 55.5 g., $[40 + (2 \times 35.5)] \div 2$. The normal solution of potassium bicarbonate, KHCO_3 , is identical with the molar. One mol of this salt is decomposed by one mol of hydrochloric acid:



In other words, one liter of normal hydrochloric acid would exactly decompose (or neutralize) an equal volume of normal potassium bicarbonate.

The following table shows the relation of the molar to the normal solution in the case of several common acids, bases, and salts. The numbers are grams per liter of solution.

Name of Substance	Formula	Molar Solution	Normal Solution
Hydrogen chloride.....	HCl	36.5	36.5
Sulfuric acid.....	H ₂ SO ₄	98.0	49.0
Acetic acid.....	H(C ₂ H ₃ O ₂)	60.0	60.0
Sodium hydroxide.....	NaOH	40.0	40.0
Potassium hydroxide.....	KOH	56.0	56.0
Sodium chloride.....	NaCl	58.5	58.5
Sodium carbonate.....	Na ₂ CO ₃	106.0	53.0
Sodium bicarbonate.....	NaHCO ₃	84.0	84.0
Aluminium nitrate.....	Al(NO ₃) ₃	213.0	71.0
Copper sulfate.....	CuSO ₄	159.6	79.8

A centi-molar solution may be abbreviated to $M/100$ or $.01 M$, and a deci-molar to $M/10$ or $0.1 M$. Likewise, a centi-normal solution may be represented by $N/100$ or $.01 N$, and a deci-normal solution by $N/10$ or $0.1 N$, etc.

166. Calculation of the Normality of a Solution. — The concentration of a solution depends, of course, upon the amount of solvent employed, as well as upon the quantity of solute. *For a given weight of solute, the concentration or normality is inversely proportional to the volume through which it is distributed.* When standard or normal solutions of certain substances have been prepared, it is possible rapidly to determine the normality of unknown solutions by measuring the volumes of the solutions which interact with each other, that is, contain amounts of the two solutes which are chemically equivalent. We may then make the calculation as follows:

$$\frac{\text{Normality of Standard Solution}}{\text{Normality of Unknown Solution}} = \frac{\text{Volume of Unknown Solution}}{\text{Volume of Standard Solution}},$$

or,
$$N : N_1 = V_1 : V.$$

Example. — 24 cc. of normal hydrochloric acid were required to neutralize 10 cc. of a solution of potassium hydroxide. Find the normality of the alkali and its concentration in grams per liter.

$$1 : N_1 = 10 : 24; \text{ whence } 10 N_1 = 24, \text{ or } N_1 = 2.4 N.$$

1 liter of a normal solution of potassium hydroxide contains 56 g. of KOH; therefore, the concentration of the alkali = $56 \times 2.4 = 134.4$ g. of KOH per liter.

167. Solution of Gases. — When two or more gases which do not interact chemically are brought together, they form a homo-

geneous mixture, which conforms to the definition of a solution. Thus, nitrogen and carbon dioxide are mutually soluble.

When dealing with a mixture or solution of gases, each gas is independent of the others, and the pressure exerted by a gas is called its **partial pressure** (49); *e.g.*, water at 22° has a vapor pressure of 19.7 mm., and a correction must be made for the partial pressure of aqueous vapor when a gas is measured over water.

While gases are soluble in each other in all proportions, their solubilities in liquids vary, depending upon the nature of the solvent and the gas, as well as upon conditions of temperature and pressure. A liquid may be saturated by bubbling a gas through it until no more of the latter dissolves.

Some gases are extremely soluble in water, others moderately soluble, and still others only slightly soluble, as shown by the table given below. The solubility of a gas is usually expressed in volumes per 1 volume of the liquid, under given conditions of temperature and pressure.

SOLUBILITY OF GASES IN 1 LITER OF WATER

Name of Gas	Volume in Liters Absorbed at 0° and 760 mm.	Volume in Liters Absorbed at 20° and 760 mm.
Ammonia.....	1300	710
Hydrogen chloride.....	506	442
Sulfur dioxide.....	79.789	39.374
Chlorine.....	2.26
Carbon dioxide.....	1.713	0.878
Oxygen.....	0.049	0.031
Nitrogen.....	0.0239	0.0164
Hydrogen.....	0.0215	0.0184

168. **Effect of Pressure and Temperature upon the Solubility of Gases.** — In 1803 W. Henry enunciated a law governing the solubility of gases.

Henry's law: At constant temperature, the weight of gas absorbed by a given volume of a liquid is proportional to the pressure at which the gas is supplied.

This law means that if a liter of water dissolves 5 g. of a gas under 1 atmosphere of pressure, it will dissolve 10 g. under 2 atmospheres.

Henry's law is approximately true for such gases as oxygen

and hydrogen; but there are numerous exceptions to the law, due to hydration, reaction with the solvent, or to other causes.

An examination of the table given above shows that gases become less soluble as the temperature rises. It is possible completely to expel air, carbon dioxide, and certain other gases from water by boiling the liquid. This may be shown by boiling water through which CO_2 has been bubbled. In the course of a short while, the amount of CO_2 escaping falls off, and finally it ceases.

169. Solution of Liquids in Liquids. — Under this head there are three cases, namely, (1) *Liquids which mix in all proportions:* e.g., water and alcohol, glycerin and water, sulfuric acid and water; (2) *liquids which are practically immiscible:* e.g., kerosene and water, benzene and water, mercury and water; (3) *liquids which are partially miscible:* e.g., ether and water. 100 g. of water dissolve 2.16 g. of ether at 22° , and 100 g. of ether dissolve 11 g. of water.

170. The Law of Partition. — If water and ether, say, 100 cc. of each liquid, are introduced into a separatory funnel (Fig. 77), a little powdered iodine added, and the mixture then shaken, the iodine will distribute itself between the two solvents, but most of it, as will be noticed by the color of the liquid, will be in the layer of ether (at the top). The ratio of the iodine concentrations in the two solvents is constant at a given temperature, which is about 200 : 1 as the experiment is ordinarily carried out. In the case of carbon disulfide and water, the ratio is about 600 : 1.

Law of Partition (Berthelot and Jungfleisch, 1872): If to two immiscible (or partially miscible) liquids, A and B, a substance be added which is soluble in both, the solute will, if its molecules are identical in both solvents, distribute itself between the two solvents so that the ratio of the concentrations in the two solvents is constant at any particular temperature.

The ratio of the concentrations is independent of the amounts of the two solvents.

There are many interesting and important applications of the law of partition, such as the Parkes process for desilvering lead (525).

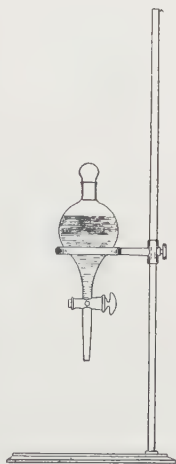


FIG. 77.

171. Solution of Solids in Liquids. — This is the most common type of solution. The solubility of solids in liquids varies greatly, being dependent upon the nature of the solute, the nature of the solvent, and upon the temperature, but is not much affected by pressure. While solubility is always limited, it varies within wide limits, as shown by the table below. In each case 100 cc. of water is saturated with the solid substance at 18°.

A liquid which has dissolved as much solute as it can from the undissolved solute at a given temperature is called a **saturated solution**; it is in equilibrium when placed with excess of solute:



SOLUBILITY OF SOME SOLID SUBSTANCES

Name of Substance	Grams of Solute in 100 cc. of Water at 18°
Silver iodide.....	0.00000035
Silver chloride.....	0.00016
Barium sulfate.....	0.00023
Calcium carbonate.....	0.0013
Lead chloride.....	1.49
Potassium chlorate.....	6.6
Sodium chloride.....	35.86
Calcium chloride.....	73.19
Silver nitrate.....	213.4
Zinc bromide.....	478.2

The first four substances in the above table are so slightly soluble in pure water that they are called "insoluble." Lead chloride is sparingly soluble in cold water, potassium chlorate moderately soluble, and such solids as silver nitrate and zinc bromide are extremely soluble.

172. Solution and the Kinetic Theory. — When a quantity of common salt, say, 50 g., is placed in a test-glass and then covered with water, say 100 cc., the salt gradually dissolves until a saturated solution is formed. Particles of salt force themselves into the liquid, *i.e.*, they exert a sort of pressure known as solution pressure. We may suppose that particles of salt are moving about in the liquid and that some of them are returning to the solid and being redeposited. When the number of particles returning to the solid is just equal to the number leaving, a state of equilibrium is reached. When the system is in equilibrium, we have a *saturated solution*.

173. Supersaturated Solutions. — When sodium thiosulfate (photographer's "hypo"), $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, is heated in a clean flask, the salt melts, or dissolves in its own water of hydration. By loosely filling the neck of the flask with clean cotton and then allowing the solution to cool to room temperature, a *supersaturated solution* is obtained, which may be kept for an indefinite period, provided the flask is not disturbed. If the cotton be removed, however, and a minute crystal of "hypo" introduced, crystallization begins at once and salt separates out until a saturated solution is formed at the particular temperature of the liquid.

Certain other salts may be used to illustrate the phenomenon of supersaturation: for example, sodium acetate ($\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$) and Glauber's salt ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$). Thus, if water be saturated with Glauber's salt, say, at 30° , and the excess of solid removed, the flask may be loosely stoppered and allowed to cool to room temperature. Upon the introduction of a minute crystal of the salt, crystallization occurs promptly.

Supersaturated solutions are said to be in the *metastable condition*; they are not in equilibrium with the solute.

The metastable condition of matter is quite common. Thus, pure water, under certain conditions, may be cooled several degrees below zero without the formation of ice.

If a given quantity of water is saturated with a certain substance, such as sodium chloride, the liquid can still dissolve other substances. This may be shown readily by shaking a saturated solution of common salt with a colored salt, like copper sulfate or potassium permanganate.

174. Effect of Temperature on the Solubility of Solids in Liquids. — Change of temperature affects the solubility of a solute. In

SOLUBILITY OF SOME COMMON SOLIDS AT DIFFERENT TEMPERATURES

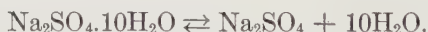
Substance	Formula	Wt. Dissolved by 100 g. of Water at		
		0°	20°	100°
Barium chloride....	$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$	31.6 g.	35.7 g.	58.8 g.
Sodium chloride....	NaCl	35.7	36.12	39.8
Potassium chloride..	KCl	27.6	34.0	56.7
Potassium nitrate...	KNO_3	13.3	31.6	246.0
Sodium nitrate....	NaNO_3	73.0	88.0	178.0
Potassium chlorate..	KClO_3	3.14	7.22	56.0
Barium hydroxide...	$\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$	1.67	3.89	101.4 (80°)
Boric acid.....	H_3BO_3	1.95	4.00	27.5
Calcium sulfate....	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	0.233	0.279 (40°)	0.26 (60°)
Calcium hydroxide..	$\text{Ca}(\text{OH})_2$	0.185	0.165	0.077

general, solids are more soluble in hot than in cold solvents, but the reverse of this is sometimes the case. Thus, $\text{Ca}(\text{OH})_2$ is more soluble in cold than in hot water. CaSO_4 is more soluble at 0° than at 100° ; its solubility increases from 0° to about 40° , where it reaches a maximum, then it decreases with rising temperature. The preceding table shows the solubility of a few common substances at different temperatures.

175. Solubility Curves. — The solubility of a substance may be shown by means of a curve (Fig. 78). The ordinates represent solubility of the solute in grams dissolved by 100 g. of water. Temperatures are represented by abscissae. If the concentration increases greatly with rise in temperature, the curve is steep: e.g., KNO_3 . The curve representing the solubility of NaCl is not steep, for rise in temperature does not have a marked effect on the solubility of common salt.

Breaks in solubility curves indicate some chemical change in the solute. Thus, the solubility curve of Glauber's salt, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, rises quite normally until a temperature of 32.4° is reached; but from this point on the curve slopes downward (Fig. 79). From 0° to 32.4° the decahydrate is in contact with water, while at temperatures above 32.4° Na_2SO_4 is present. Glauber's salt, therefore, becomes anhydrous at 32.4° , which is called a **transition point**. We have one solubility curve for the hydrate and a different one for the anhydrous salt.

$$32.4^\circ$$



176. Influence of Solute upon Solvent. — Solutions have freezing points, boiling points, and vapor pressures which differ from those of the pure solvent. They also exhibit, under proper conditions, osmotic pressure. These changes occur with regularity in the case of very dilute solutions, particularly when solids are dissolved in liquids. The three classes of compounds called acids, bases, and salts do not behave in the regular or normal way; they will receive special consideration in a subsequent chapter (see Ionization).

177. Freezing Points of Solutions. — *A mol of such substances as cane sugar ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$), glucose ($\text{C}_6\text{H}_{12}\text{O}_6$), and alcohol ($\text{C}_2\text{H}_6\text{O}$), when dissolved in 1,000 g. of water, lowers the freezing point approximately 1.86° , which is the depression constant for water.*

The laws of freezing point depression may be stated thus:

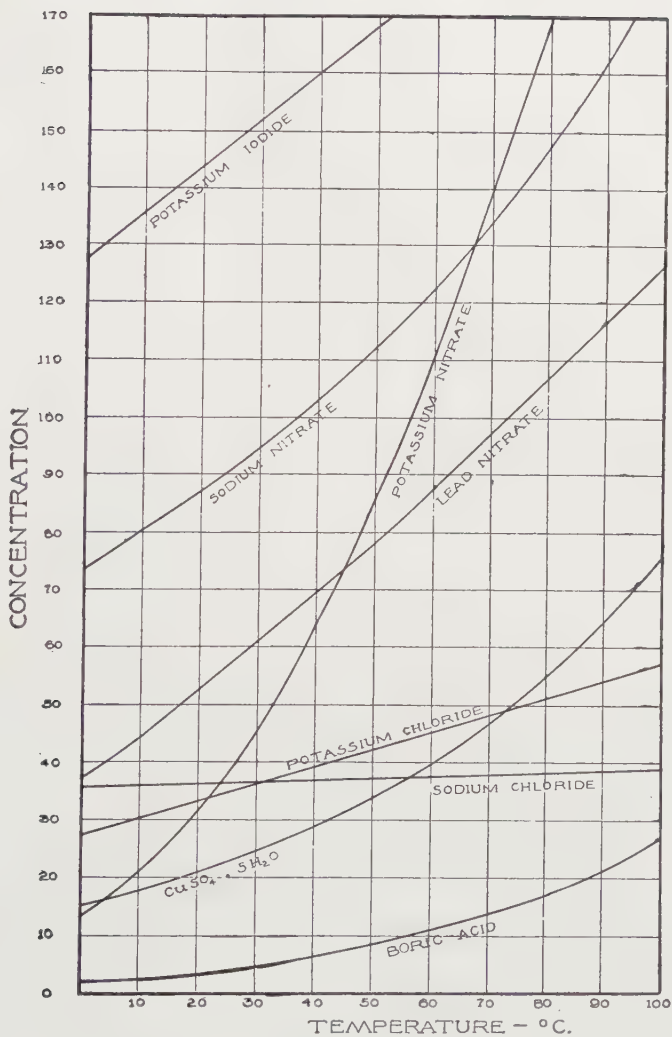


FIG. 78.

(1) The depression is proportional to the concentration (C. Blagden, 1787).

(2) Equal numbers of molecules of different solutes in the same quantity of solvent produce equal depressions (F. M. Raoult,

1883). Thus, 342 g. of cane sugar or 46 g. of alcohol, when added to 1,000 g. of water, depress the freezing point 1.86° .

Molecular weights of soluble substances like the sugars and hydrogen peroxide may be measured by the freezing point method.

The Beckmann apparatus is very generally used for determining molecular weights by the freezing point, or cryoscopic, method. It consists of a tube *A* with a side-tube, which is sunk into a wider tube in order to surround the former by an air space (Fig. 80). A heavy glass jar *C* contains a freezing mixture which is stirred by the stirrer *D*. The inner tube is fitted with a Beckmann thermometer and a stirrer. A known weight of

CONC.

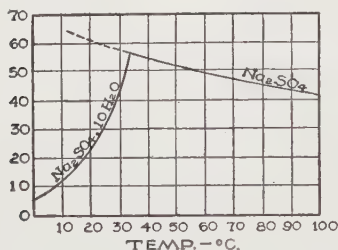


FIG. 79.

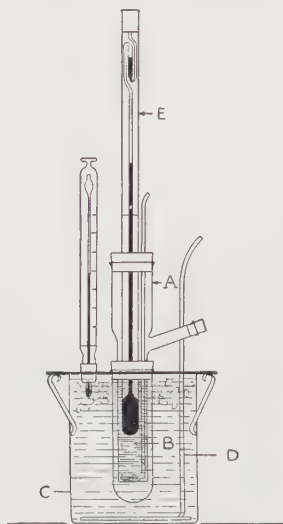


FIG. 80.

the solvent is placed in tube *A*, its freezing point determined, and then a weighed quantity of the solute is introduced through the side-tube, and the freezing point of the solution (*B*) determined. The difference between this number and the freezing point of the pure solvent gives the depression of the freezing point.

The observed depression (Δ) in an aqueous solution may be expressed thus:

$$\Delta = 1.86^{\circ} \times \frac{\text{Wt. of Solute}}{\text{Mol. Wt. of Solute}} \times \frac{1000}{\text{Wt. of Solvent}}$$

In the case of other solvents, the corresponding value of the "depression constant" is substituted for 1.86° . Thus, for benzene we use 5.1° and for acetic acid 3.9° .

The following general formula may be employed:

$$\Delta = \delta \times \frac{W \times 1000}{M \times g},$$

in which δ is the depression produced by 1 mol of the solute in 1,000 g. of the solvent, W the weight of the solute, M its molecular weight, and g the weight of the solvent. From this expression, in the case of the solvent water, we have:

$$M = \frac{1860 W}{\Delta g}.$$

Example. — 0.340 g. of a substance dissolved in 10.5 g. of water gave a depression of 0.20° . Calculate the molecular weight of the substance.

What does the expression $\frac{W}{M}$ represent?

It has been known since the time of Aristotle that it is possible to obtain drinkable water from the ice of frozen sea-water. The accompanying diagram (Fig. 81) shows that when a salt solution is gradually cooled, comparatively pure ice first separates. Pure water freezes at 0° , while salt solutions freeze at lower temperatures.

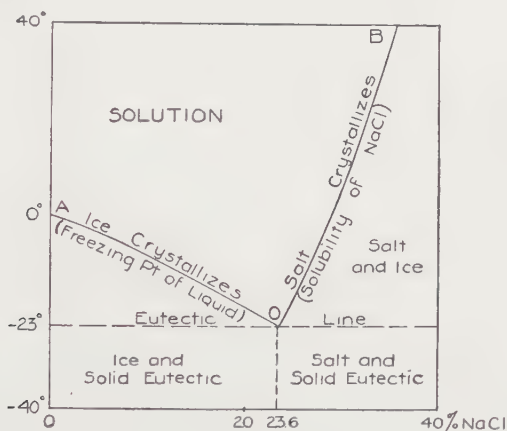


FIG. 81. Solubility and Freezing Curves of NaCl in Water.

This is shown by the “ice line” AO. When dilute brine is cooled to the freezing point, ice separates out and the concentration of the solution increases until it contains 23.6 per cent of salt and the freezing point is -23° . At this temperature the remaining liquid freezes *en masse*. On the other hand, if we lower the temperature of a salt solution containing more than 23.6 per cent of NaCl, pure salt separates out until the liquid contains 23.6 per cent of NaCl and the temperature falls to -23° . This is shown by the “salt line” BO. If the brine which is being cooled contains just 23.6 per cent of NaCl, neither ice nor salt separates out until the temperature is reduced to -23° , when the liquid freezes *en masse*. No other solution of salt freezes at a lower temperature than this; therefore, a solution containing 23.6 per cent of NaCl is known as a **eutectic mixture** (Greek, meaning *easily melted*), and -23° is the eutectic temperature.

178. Elevation of the Boiling Point. — *A mol of a substance like sugar, when dissolved in 1,000 g. of water, raises the boiling point approximately 0.52° . The solute interferes therefore with the formation of vapor, so that the vapor pressure curve of the pure solvent is higher than that of a solution (Fig. 82).*

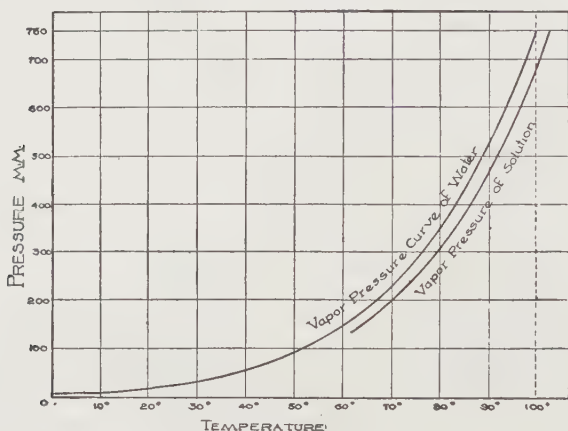


FIG. 82.

Molecular weights of certain substances in solution may be determined by the boiling point method. The method cannot be successfully employed for volatile substances, such as benzene and the common alcohols.

179. Lowering of the Vapor Tension of the Solvent. — We have just seen that the presence of a solute elevates the boiling point of a solvent. This means that the vapor pressure is lowered. The lowering of the vapor pressure is proportional to the concentration of the solution; it is independent of the chemical properties of the solute, being dependent solely upon the number of molecules.

The lowering of the vapor pressure of solutions enables us to explain **deliquescence**. When certain very soluble substances, such as the chlorides of magnesium, calcium, and zinc, are exposed to the air, they first become moist, and finally go into solution. This is due to the fact that when the solid comes in contact with the moisture in the air, water is absorbed and a very concentrated solution is formed on the surface of the crystal. As the vapor tension of this solution is less than the partial pressure of the

water vapor in the air, more moisture is taken up from the air until the solid goes entirely into solution. As more water is absorbed, the solution becomes more dilute. This deportment of certain substances is known as deliquescence.

The following *experiment* will make the principle clear:

Two beakers of the same size were selected and one (A) was filled half full of distilled water and an equal volume of a concentrated solution of magnesium chloride was introduced into the other beaker (B). The vessels were placed under an air-tight bell-jar standing at room temperature on a plate of glass. Water gradually evaporated from vessel (A) and was condensed or absorbed in vessel (B). At the end of four years the relative volumes of the liquids were as represented in Fig. 83.

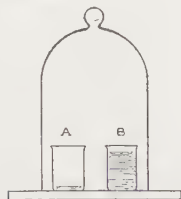


FIG. 83.

Common salt usually contains more or less magnesium chloride, which deliquesces, particularly when the weather is hot and the air humid.

180. Osmosis and Semipermeable Membranes. — When plants grow, water and soluble salts of the soil are taken up by the moist walls of the root-hairs and they circulate through the plants from cell to cell. The salts of nutritive value to the plants interact with the contents of the cells to form complex organic substances which are unable to permeate the membranes of the cells, while the salts of no nutritive value are rejected. Both the rejected salts and water can pass through the membranes in both directions, water circulating more freely. The passage of water and soluble salts into the cells is termed **osmosis** (Greek, meaning *impulsion*). As the membranes of the cells are permeable to water, but not to the complex substances inside, they are said to be semipermeable. The life of a plant is dependent upon its ability to select from the soil (as well as from the air) those substances required for its growth. Osmosis is therefore of great importance in the study of plant physiology; also animal physiology.

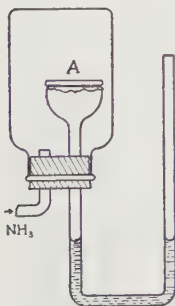


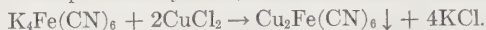
FIG. 84.

Osmosis and semipermeable membranes may be illustrated by means of the following *experiments*:

Experiment 1. — A funnel-tube is fitted to a stopper and then bent so as to form a manometer as shown in Fig. 84. An animal membrane is stretched over the mouth of the funnel and carefully tied on. The bent part of the tube is then filled with an oil and colored with a small amount of a dye so

as to make it readily visible. The stopper is now fitted to an inverted bottle to which ammonia gas (NH_3) is admitted. The membrane allows ammonia to pass both ways, but does not allow air to escape. Ammonia diffuses until the pressure of this gas is the same on both sides of the membrane. Since the air cannot escape, there is an excess of pressure inside the funnel-tube, which causes the oil to rise in one side of the tube.

Experiment 2. — About 7.5 g. of potassium ferrocyanide, $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$, are dissolved in 100 cc. of distilled water contained in a beaker. A few small crystals of a cupric salt (*e.g.*, the chloride) are carefully dropped into the solution. These crystals sink to the bottom, and are soon covered by a thin membrane of cupric ferrocyanide, a reddish-brown insoluble salt:



This compound serves as a semipermeable membrane, allowing water to pass freely, but preventing the escape of the copper salt. As a consequence, osmosis goes on until fairly large balloon-like forms are to be seen. In case the pressure becomes too great, the membranes are ruptured and then collapse.

Experiment 3. — The metal palladium, at a temperature of 300° , is permeable to hydrogen but not to nitrogen. If a vessel constructed of palladium were filled with nitrogen at atmospheric pressure, closed, and then immersed in a second vessel containing hydrogen at a constant pressure of one atmosphere, the hydrogen would permeate the walls of the palladium until the hydrogen pressure is the same on both sides; that is, one atmosphere. The total pressure, therefore, inside the palladium vessel would be two atmospheres — one due to the hydrogen and the other to the nitrogen. Both gases exert their normal pressures on the inner walls of the palladium vessel.

181. Osmotic Pressure. — That there is a pressure in solutions may be demonstrated by the following *experiment*:

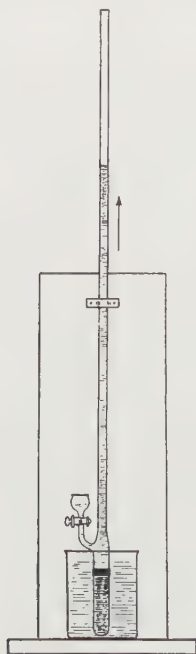


FIG. 85.

A diffusion shell is fitted to the enlarged end of an open glass tube, as shown in Fig. 85. A sugar solution is run into the diffusion shell through the small funnel attached to the side of the tube, the stop-cock closed, and the shell immersed in a vessel containing water. In the course of time, liquid rises in the tube; for the diffusion shell allows water to pass freely, but very little sugar passes through. In other words, the diffusion shell is a semipermeable membrane. The rise of

liquid in the tube demonstrates that a pressure is exerted. The column of liquid will rise, if the semipermeable membrane be strong enough, until the hydrostatic pressure produced is just equal to the force tending to drive water into the vessel. This pressure is called the osmotic pressure, and is caused by the force tending to produce equilibrium between pure water (the solvent) and solution which, in the absence of a membrane, results in mixing by diffusion, a homogeneous solution being produced.

Diffusion shells are not ordinarily strong enough to enable one to measure osmotic pressure. Pfeffer (1877) and others have constructed special cells adapted to the quantitative determination of osmotic pressure. Pfeffer treated porous cylinders with potassium ferrocyanide and a cupric salt, so as partially to fill their pores with cupric ferrocyanide (see Experiment 2, above).

Very careful measurements show that the *osmotic pressure of a dilute solution is proportional to the concentration and the absolute temperature*; also, that the osmotic pressure exhibited by a substance is somewhat analogous to the gaseous pressure the substance would exert if it existed as a gas at the same temperature and were confined in the same volume. The laws governing osmotic pressure hold only for very dilute solutions.

The experiments described in the previous section may aid in giving us some sort of mental picture as to the cause of osmotic pressures; it is a consequence of osmosis.

Abbé Nollet, in 1748, was the first to observe the process of osmosis. He showed that if a sugar solution be placed in a vessel (*e.g.*, an inverted funnel-tube) which is closed below by an animal membrane and then dipped in a vessel containing water, the solution will rise in the vessel, due to the passage of water through the membrane. This experiment may be easily performed by firmly stretching a piece of gold beater's skin over the mouth of a funnel-tube, fastening it on with a strong thread, and then making the joint tight by means of marine glue or sealing wax. The enlarged portion of the tube is now filled with a concentrated sugar solution, immersed in a vessel of distilled water, and clamped in the vertical position (Fig. 86).

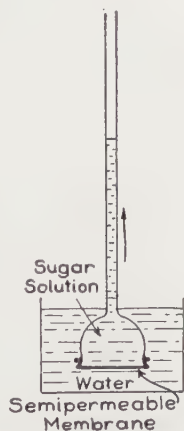


FIG. 86.

182. Heat of Solution. — When a substance goes into solution, heat is, as a rule, either evolved (positive) or absorbed (negative). This is called heat of solution. To illustrate, one mol of sulfuric acid (98 g.), in dissolving in a large volume of water, sets free 39,170 calories. Such substances as ammonium nitrate and ammonium chloride absorb heat in dissolving in water. As a general rule, solid substances absorb heat during the process of solution, while during the process of crystallization heat is usually evolved (173).

EXERCISES

1. State all the differences you can between true solutions, fine suspensions (colloidal solutions), and coarse suspensions. What is an emulsion?

2. Define, and also illustrate fully, the following: (a) molar solution, (b) normal solution, (c) normal solution of an acid, (d) normal solution of a base, (e) normal solution of a salt.

3. If 37 g. of barium hydroxide are present in 5 liters of a solution, what is (a) the molar concentration and (b) the normal concentration?

4. If 2.45 g. of H_2SO_4 are present in 1 liter of a solution, what is (a) the molar concentration and (b) the normal concentration?

5. 45.5 cc. of $N/2$ sodium hydroxide were required to neutralize 10 cc. of white vinegar (acetic acid). Find the strength (normality) of the vinegar and the number of grams of acetic acid per liter of the liquid.

6. 30.6 cc. of normal hydrochloric acid were required to neutralize 10 cc. of a solution of sodium carbonate (Na_2CO_3). What was the weight of salt per liter of solution? What was the normality of the salt?

7. How many mols of sulfuric acid could be neutralized by 5 gram-equivalent weights of potassium hydroxide?

8. State Henry's law. Justify the following statement: "Under equal circumstances of temperature, a given volume of water takes up in all cases the same volume of a condensed gas as of a gas under ordinary (atmospheric) pressure."

9. State the law of partition. Give an application of the law. Ether is a solvent for butter-fat. Could the law of partition be applied to the extraction of butter-fat from milk? If so, how would you proceed?

10. Explain the following: (1) saturated solution; (2) supersaturated solution; (3) the break in the solubility-curve of Glauber's salt; (4) deliquescence.

11. Describe a method by which you would determine the solubility of sodium chloride in water at any particular temperature. How would you determine the "total solids" in drinking water?

12. What is the effect of a solute upon the properties of a solvent? What relation has the number of molecules to the freezing point, osmotic pressure, etc.?

13. From the following data draw the solubility curves of the substances. The solubilities are to be expressed in grams in 100 g. of water.

	0°	10°	20°	40°	60°	80°	100°
(1) Potassium chloride.	27.6	31.0	34.0	40.0	45.5	51.1	56.7
(2) Barium nitrate. . . .	5.0	7.0	9.2	14.2	20.3	27.0	34.2
(3) Lithium carbonate. . .	1.54	1.43	1.33	1.17	1.01	0.85	0.72

14. If the radiator of an automobile contains 15 liters (kilograms) of water, how much would the freezing point be lowered by the addition of 5 kilograms of ethyl alcohol ($\text{C}_2\text{H}_5\text{O}$)? How many kilograms of methyl alcohol (CH_4O) would be required to produce the same result?

15. Explain how a rubber bottle filled with a supersaturated solution of sodium acetate can be employed as a sort of hot-water bottle.

16. When solid paraffin is dissolved in gasoline, the heat absorbed is practically identical with the heat required to melt the same quantity of the solid. Furthermore, when gasoline is mixed with paraffin in the liquid state, there is no observable heat effect or volume change. Would you regard this change in dissolving as chemical or physical?

17. The physical properties of water indicate that it contains complex molecules formed by the combination of simple H_2O molecules:



Do you think that dissolving in water is a physical or a chemical change?

18. How many times normal is each of the following solutions: 0.1 molar Na_3PO_4 ; 3 molar H_2SO_4 ; 2.5 molar MgCl_2 ; 0.5 molar cupric sulfate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$?

19. (a) What is the normality of a solution of HCl containing 39 per cent by weight of HCl and of density 1.19?

(b) The density of a 77 per cent solution of sulfuric acid is 1.7. What is its normality?

20. If 5 g. of a substance, dissolved in 1000 g. of water, gave a solution freezing at -0.2°C ., what is the molecular weight of the substance?

21. The freezing point of a 3.3 per cent solution of hydrogen peroxide in water was found to be -2.03°C . Calculate the depression produced by 3.3 g. of hydrogen peroxide in 1000 g. of water, and from the value thus obtained find out the weight of hydrogen peroxide required to produce a depression of 1.86°C . in 1000 g. of water, and then assign the formula to the compound. *Ans.* -0.196°C . and 31.3 g.

22. Explain why salt will melt ice on a fairly cold day.

23. What is meant by osmosis? Show how osmotic pressure may be demonstrated.

READINGS AND REFERENCES

CHAPIN. Second Year College Chemistry, Chaps. XII and XIII.

SMITH-KENDALL. Inorganic Chemistry, Chap. XII.

TAYLOR. Elementary Physical Chemistry, Chap. VIII.

CHAPTER X

MOLECULAR WEIGHTS AND ATOMIC WEIGHTS; MOLECULAR FORMULAE

MOLECULAR WEIGHTS

183. **Importance of Avogadro's Generalization.** — The fundamental law of Gay-Lussac relating to the volumes of gases (152), was explained by the Hypothesis proposed by Avogadro in 1811 (55). If we assume that equal volumes of different gases under the same conditions contain the same number of molecules, two important conclusions follow:

(1) *A molecule of one gas occupies the same average space as a molecule of any other gas.* This statement does not imply that molecules of different gases are necessarily of the same size. To illustrate, we might imagine a number of individual cells of the same dimensions, and each cell containing an object. It is easy to see that the objects might be of different sizes. The individual molecules of gases are very small as compared with the average space assigned to them. The volume of a gas is, therefore, proportional to the number of molecules which it contains.

(2) *The molecular weights of gases are proportional to their densities.*

This relationship may be arrived at as follows:

Let n equal the number of molecules in 1 cc. of any gas at S.T.P.; then nm = the weight of 1 cc. of a gas having a molecular weight m , and nm_1 = the weight of an equal volume of a gas having a molecular weight of m_1 . It now follows that —

$$\frac{m}{m_1} = \frac{nm}{nm_1} = \frac{d}{d_1}; \quad \text{or} \quad \frac{m}{m_1} = \frac{d}{d_1}.$$

This is the most important deduction from Avogadro's generalization, for it gives us a method for the determination of the molecular weights of gases.

The hypothesis of Avogadro, which was enunciated in 1811, was not fully appreciated until after 1858. In that year the Italian chemist, Cannizzaro, published a pamphlet, which cleared up certain obscurities. Before the publication of his paper on chemical philosophy, there was great confusion as to the exact

meaning of "atomic weights," "combining weights," and "molecular weights."

It will be shown subsequently that the determination of molecular weights leads to the determination of atomic weights.

184. Molecular Weights. — We have just seen that the relative weights of the individual molecules of different gases, *i.e.*, their molecular weights, are proportional to their densities.

If we could count out and arrange in piles an equal number of molecules of two different gases, say, oxygen and carbon dioxide, it is evident from what has been said that the weights of the two piles of molecules would be related to each other as the weights of their individual molecules. Since this cannot be done by a direct method, it is done indirectly by comparing the weights of equal volumes of the different gases; for the weights of equal volumes of gases are proportional to their densities, and hence to their molecular weights. To complete the method for arriving at the relative weights of the molecules, a *standard* is required to which all chemical weights are to be referred. Now, the choice of a standard is purely arbitrary. Dalton chose hydrogen, and Berzelius oxygen. For the best of reasons oxygen is now the usual standard, and 32 is the molecular weight assigned to it.

Our chemical scale of molecular weights will be calculated to the scale, molecular weight of oxygen = 32. We may now write:

$$d : d_1 = m : m_1; \text{ or,}$$

$$\text{Density of Oxygen : Density of Any Other Gas} = 32 : m.$$

Example. — The weight of a liter of oxygen, at S.T.P., is 1.429 g., and that of carbon dioxide is 1.965 g. Find the molecular weight of the latter.

As the weights of liters of gases may be taken as their densities, we have:

$$1.429 : 1.965 = 32 : m_1; \text{ therefore,}$$

$$m_1 = 32 \times \frac{1.965}{1.429} = 44,$$

the molecular weight of carbon dioxide referred to oxygen = 32.

As the gram is the chemical unit of weight, 32 g. of oxygen and 44 g. of carbon dioxide are the gram-molecular weights of these substances respectively. For the sake of brevity, the **gram-molecular weight** is often called the **molar weight**, or **mol**.

185. The Gram-molecular Volume: 22.4 liters. — As 32 has been chosen as the molecular weight of oxygen, a gram-molecular

weight of the gas is 32 g. What volume, at S.T.P., do 32 g. of oxygen occupy? $32 \div 1.429$ (the weight of 1 liter) = 22.4 liters. This volume is called the gram-molecular (molar) volume of gases, and it is the unit of volume for gases. It is the same (ap-



FIG. 87.

proximately) for gram-molecular weights of all gases. Thus, for carbon dioxide, $44 \div 1.965 = 22.4$. The gram-molecular volume is abbreviated to G.M.V. A cube 28.19 cm. (= 11.1 in.) in height holds 22.4 liters (Fig. 87).

186. Determination of Molecular Weights. —

The determination of the approximate molecular weight of a substance resolves itself into the problem of finding the weight in grams of the gas or vapor required to fill the same volume as 32 g. of oxygen at S.T.P., *i.e.*, 22.4 liters.

From the proportion, $1.429 : 1.965 = 32 : m_1$, it follows that $m_1 = \frac{32}{1.429} \times 1.965 = 22.4 \times 1.965 = 44$. Stated in words, it reads that the molecular weight in grams of any gaseous substance may be found by multiplying the weight of one liter of the gas, at S.T.P., by the constant 22.4; or, mol. wt. = $22.4 \times$ wt. of 1 liter of the gas. This does not mean that the chemist has to weigh out any particular volume of the gas at any particular temperature and pressure. Instead, he weighs a known volume of the substance at any temperature and pressure at which it is gaseous, and then reduces the volume to S.T.P. From this it is simple to calculate the weight of 22.4 liters of the gas or vapor.

Example. — 111.4 cc. of a gas, measured dry and at 27° and 750 mm., weigh 0.1537 g. What is its molecular weight?

$$V_{\text{(S.T.P.)}} = 111.4 \times \frac{273}{300} \times \frac{750}{760} = 100 \text{ cc.}$$

100 cc. weigh 0.1537 g., or 1 liter weighs 1.537 g.; therefore, 22.4 liters weigh $22.4 \times 1.537 = 34.43$ g., the gram-molecular weight.

It should be clearly understood that Avogadro's law enables the chemist to arrive at the molecular weights of gases by dealing with masses of gases containing very large numbers of molecules. Dealing with equal volumes of gases is equivalent to dealing with the individual molecules, for equal volumes contain the same number of molecules (Avogadro's law). Thus, 22.4 liters of oxygen contain the same number of molecules as 22.4 liters of

carbon dioxide, etc. In other words, the weights of 22.4 liters of two gases are to each other as the weights of their individual molecules.

It follows from what has been said that the approximate weight of a liter of any gas or vapor can be found by dividing its gram-molecular weight by 22.4:

$$\text{Wt. of 1 Liter of a Gas} = \frac{\text{Gram-molecular Weight}}{22.4}.$$

187. Formulae for Calculating Molecular Weights. — Problems are frequently stated in which the molecular weights are to be found by referring the relative densities of the gases to hydrogen or air instead of oxygen.

(1) When the relative density (sp. gr.) is referred to *oxygen*, the formula is

$$\text{Mol. Wt.} = 32 \times \frac{\text{wt. of 1 liter of the gas}}{\text{wt. of 1 liter of oxygen}} \quad (184).$$

But the weight of 1 liter of a gas divided by the weight of 1 liter of the standard gas is its *relative density*, or *sp. gr. (d)*. Our formula may now be written

$$\text{Mol. Wt.} = 32 d.$$

(2) For *hydrogen*, we have

$$\text{Mol. Wt.} = 2 d; \text{ for}$$

2 g. (approximately) of hydrogen are required to fill the G.M.V., and *d* in this case is the sp. gr. of the gas referred to hydrogen. We may now write:

$$\text{Mol. Wt.} = 2 \times \frac{\text{wt. of 1 liter of the gas}}{\text{wt. of 1 liter of hydrogen}}.$$

From the expression, $\text{Mol. Wt.} = 2 d$, it follows that, $d = \frac{\text{Mol. Wt.}}{2}$.

d in this case is usually called the *vapor density*, which is identical with the sp. gr. of the gas referred to hydrogen taken as 1.

(3) Since the G.M.V. of pure dry *air* weighs, at S.T.P., 28.955 g., it is easy to see that $\text{Mol. Wt.} = 28.955 d$, in which *d* is the sp. gr. of the gas, air being taken as 1.

Example. — (a) The relative density of a gaseous compound (oxygen = 1) is 2.5. Find its molecular weight.

(b) The relative density of a gas (hydrogen = 1) is 15. Find its molecular weight.

(c) The relative density of a gas (air = 1) is 1.52. What is its molecular weight?

$$(a) \text{ Mol. Wt.} = 32 d = 32 \times 2.5 = 80.$$

$$(b) \text{ Mol. Wt.} = 2 d = 2 \times 15 = 30.$$

$$(c) \text{ Mol. Wt.} = 28.955 d = 28.955 \times 1.52 = 44 \text{ (nearly).}$$

Note that 32 g. of oxygen, 2 g. of hydrogen (approximately) and 28.955 g. of pure, dry air occupy the same volume, namely, 22.4 liters.

188. Determination of Vapor Density. — The molecular weights of volatile liquids (and solids) may be determined by first finding the density of their vapors. Two methods for the determination of vapor density are briefly outlined below, namely, the Dumas method and the Victor Meyer method.

Dumas' Method (1826) consisted in volatilizing a few grams of the substance by heating it in a light glass bulb with a long neck. When the bulb was full of vapor, the neck was sealed and the weight of the vapor and the volume of the bulb determined.

In **Victor Meyer's Method** (1877) the volume of a vapor is found by measuring the volume of air displaced by the vapor of a known weight of the volatile substance. The method is best explained by means of the accompanying diagram (Fig. 88). The apparatus consists of an inner tube *B* surrounded by an outer tube or jacket *A*, in the bottom of which is placed a substance with a boiling point 30° or more higher than that of the liquid the vapor density of which is to be determined. A small closed bottle (or bulb) containing a known weight of the liquid is introduced into the inner tube by removing the stopper, being

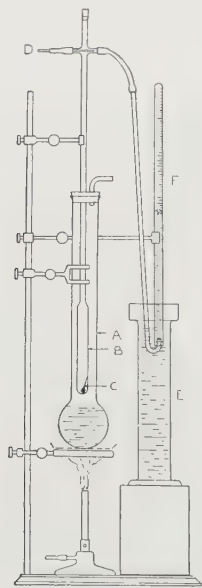


FIG. 88.

arrested by a movable shelf placed at *D*. The tube is tightly stoppered, the liquid in the bulb of the jacket boiled until the temperature of the inner tube is constant, the expanding air being allowed to escape through the side-tube into the atmosphere. When

no more bubbles of gas escape from the end of the delivery tube, the graduated tube *F* containing water (or mercury) is clamped in position. The shelf *D* is now pulled aside and the little bottle containing the liquid falls to the bottom of the inner tube. The liquid vaporizes rapidly and blows the stopper out of the bottle, and the rising vapor displaces its own volume of air which collects in the tube *F*. This volume of air is now measured at atmospheric pressure, and the temperature and barometric pressure noted. From these data and the weight of the liquid undergoing vaporization the density of the vapor may be readily calculated, and from this value the molecular weight found.

Example. — 0.150 g. of chloroform was volatilized by means of boiling water, and the resulting vapor displaced 30.5 cc. of air, measured over water at 22° C., the barometric pressure being 755 mm. Find the vapor density of chloroform and then calculate its molecular weight.

Note. — First find the volume of dry air at S.T.P., which corresponds to the volume of 0.150 g. of chloroform vapor under the same conditions. Chemical analysis shows that the formula of chloroform is $(\text{CHCl}_3)_x$, in which *x* is a whole number.

Both the Dumas and the Victor Meyer methods have undergone modification since they were discovered. The latter method is much more convenient.

It is understood, of course, that the vapor density method cannot be employed for the determination of the molecular weights of unstable substances like the sugars. Since these compounds and many others are soluble, their molecular weights may be determined by other methods, such as the freezing point method (177).

189. Avogadro's Constant, N. — The number of molecules in gram-molecular weights of different gases is the same, provided we grant the validity of Avogadro's hypothesis. This number, *N*, is called Avogadro's number or Avogadro's constant. How many molecules are there, therefore, in 22.4 liters of a gas at S.T.P.?

This number has been found by several different methods (70), which have given results that agree remarkably well. Millikan found the value 6.06×10^{23} , or 606 sextillion molecules (606 followed by 21 ciphers). It would take 1,000,000,000 people each counting 24 hours every day, at the rate of 3 per second, nearly 6,500 years to count this number! A gram-atom contains 6.06×10^{23} atoms (128).

ATOMIC WEIGHTS

The atomic weights of the different elements are the relative weights of the atoms. The number 16 has been assigned to oxygen (30), and other atomic weights are based on this number. The problem is, therefore, to determine the relative weights of the elements based on oxygen = 16. If 16 g. of oxygen are taken, we have 1 gram-atomic weight of the element. Likewise, gram-atomic weights of other elements are the atomic weights of the elements expressed in grams.

190. Method for the Determination of Atomic Weights Based upon Avogadro's Law. — At the outset we may define the atomic weight of an element thus: It is the smallest weight in grams of the element ever found in the gram-molecular weight, *i.e.*, in 22.4 liters at S.T.P., of any volatile compound containing the element. In other words, we are seeking the atomic weight expressed in grams. We select the smallest weight of the element in the G.M.V., for the atom is defined as the smallest particle in the molecule.

The following steps are to be taken:

(1) *Find the molar weights (M) of a number of gaseous or volatile compounds containing the element, i.e., the weights of the gaseous substances required to occupy 22.4 liters at S.T.P.*

(2) *Determine by analysis the percentage of the element present in each of the compounds.*

(3) *Calculate the weight of the element in the gram-molecular weight as follows: 100 per cent : per cent El. = M : Wt. of El. in the Mol.* This gives the number of grams of the element in the mol.

(4) *Take the highest common factor of the weights found in (3), or the smallest weight of the element found in 22.4 liters of any of its volatile compounds.* This number represents the *approximate* atomic weight of the element.

(5) The Exact Atomic Weight = Equivalent Weight \times Valence (133).

The following table will illustrate the various steps. The problem is to find the exact atomic weight of carbon.

We see in the last column that the average of the smallest weights of carbon found in the gram-molecular weights is 12.15 g., so we may regard 12.15 as the approximate atomic weight of carbon. The other numbers are multiples (approximately) of 12.15.

The final step is to find the *exact* atomic weight of carbon. Chemists have found by very accurate experiments that the equivalent weight of carbon is 3.000. This number multiplied by the valence of carbon will give the atomic weight sought. The approximate atomic weight (12.15) is close enough to enable us to decide upon the valence, for it is a whole number obtained by dividing the atomic weight by the equivalent weight. The valence of carbon is, therefore, 4, so its exact atomic weight is $3.000 \times 4 = 12.000$.

TABLE ILLUSTRATING THE DETERMINATION OF ATOMIC WEIGHTS

Name of Compound	Molar Weight M	Per cent of Element	Weight of Element in Mol
Carbon monoxide.....	28.0	42.9	12.0
Carbon dioxide.....	44.3	27.3	12.1
Methane.....	16.0	74.9	12.0
Acetylene.....	25.8	92.3	23.8
Benzene.....	77.6	92.3	71.6
Carbon disulfide.....	76.9	15.8	12.2
Carbon tetrachloride.....	154.0	7.8	12.1
Chloroform.....	120.0	10.4	12.5
Alcohol.....	46.6	52.2	24.3

The method just developed applies only to elements such as carbon, chlorine, and nitrogen that form a considerable number of stable gaseous or volatile compounds. If a compound should ever be discovered containing 6 g. of carbon in the mol, *i.e.*, in 22.4 liters of the gas at S.T.P., the atomic weight of carbon would be reduced to one-half of its present value; but it is not likely that such a discovery will be made.

191. Method for the Determination of Atomic Weights Based Upon the Law of Specific Heats. — This method is applicable to *solid elements* only, such as gold, platinum, silver, iron, and tin.

In 1818 Dulong and Petit, of Paris, enunciated the **Law of Specific Heats**, which may be stated thus:

The product of the atomic weight and the specific heat of a solid element is approximately constant.

In other words, the atoms have the same capacity for heat. It has been found that the mean value for the constant is about 6.4.

$$\text{Atomic Weight} \times \text{Specific Heat} = 6.4 \text{ (nearly);}$$

therefore,

$$\text{Atomic Weight} = 6.4 \div \text{Specific Heat.}$$

6.4 is called the **atomic heat** of an element.

TABLE OF SPECIFIC AND ATOMIC HEATS OF SOME SOLID ELEMENTS

Element	Atomic Weight	Specific Heat	Atomic Heat
Lithium.....	6.94	0.9063	6.29
Sodium.....	23.00	0.2829	6.51
Iron.....	55.84	0.1189	6.64
Silver.....	107.88	0.0590	6.36
Tin.....	118.70	0.0551	6.55
Platinum.....	195.23	0.0323	6.31
Gold.....	197.20	0.0330	6.51
Lead.....	207.22	0.0310	6.42
Uranium.....	238.17	0.0280	6.67

By examination of the table it may be seen that the specific heat decreases as the atomic weight increases, and that *equal amounts of heat will raise atomic weights of the solid elements through equal intervals of temperature*. There are a few notable exceptions, however, — boron, carbon, beryllium, and silicon. Their specific heats are abnormally low, but at high temperatures they approach the number 6.4, although that value has not been attained.

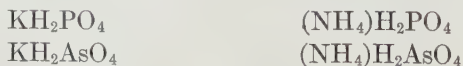
The law of Dulong and Petit is a rough, empirical rule for the determination of atomic weights of certain of the solid elements, particularly metals.

Example. — We know from analytical considerations that the atomic weight of cadmium is 56.2 or some multiple of 56.2. The specific heat of cadmium is 0.0568. Find the exact atomic weight of the metal.

At. wt. = $\frac{6.4}{\text{sp. ht.}} = \frac{6.4}{.0568}$, or 114.3, the approximate atomic weight. As 56.2 is the equivalent weight of cadmium, its valence is 2; consequently the exact atomic weight is $56.2 \times 2 = 112.4$.

192. Isomorphism. — In 1819 E. Mitscherlich enunciated a law called the **Law of Isomorphism**, namely: **Substances which have similar chemical composition generally crystallize in the same system and exhibit the same forms.**

To illustrate, Mitscherlich observed that the acid phosphates and arsenates of potassium and ammonium are **isomorphous** (Greek, meaning *equal + form*), as represented by the following pairs of formulae:



In these compounds one element or radical may be exchanged for another: *e.g.*, phosphorus may be exchanged for arsenic, and

potassium for ammonium, without affecting the crystalline form. A phosphate, therefore, has its corresponding arsenate.

In certain cases solid substances which have similar chemical character and crystalline form, blend together to form homogeneous mixtures, very much as sugar blends with water to form a solution (5). *Isomorphous mixtures are solid solutions.*

The tests for isomorphism are as follows:

- (1) Similarity of crystalline form (Mitscherlich);
- (2) Formation of mixed crystals (Retgers);
- (3) Formation of overgrowths (Kopp).

Substances answering to these tests are generally isomorphous, but none of these is an infallible criterion of isomorphism.

When a solution containing potash alum and chrome alum (588) is allowed to crystallize, the crystals are an isomorphous mixture, *i.e.*, a solid solution, of the two alums. The product has properties intermediate between the two pure alums.

Besides those already mentioned, other isomorphous compounds are:

- (1) Al_2O_3 , Fe_2O_3 , Cr_2O_3 , Ti_2O_3 .
- (2) The vitriols: $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$.
- (3) CaCO_3 (aragonite), SrCO_3 , BaCO_3 , PbCO_3 .
- (4) SrSO_4 , BaSO_4 , PbSO_4 .
- (5) PbS and Ag_2S .
- (6) Perchlorates and permanganates.
- (7) Sulfates and chromates.
- (8) Sulfates and selenates.

The law of isomorphism has been of service in the **determination or rectification of atomic weights**. Thus, Berzelius arrived at the number 79 as the atomic weight of selenium. Potassium sulfate and potassium selenate are isomorphous. Analysis of these compounds gave:

	K	O	S	Se	Total
Potassium sulfate	44.83	36.78	18.39	100.00
Potassium selenate ¹	44.83	36.78	45.40	127.01

Given the atomic weight of sulfur as 32, and assuming that the molecule of potassium sulfate contains 1 atom of sulfur, while

¹ The percentage composition of potassium selenate is: Potassium, 35.29; selenium, 35.75; oxygen, 28.96. These numbers are related to one another as those given above.

that of potassium selenate contains 1 atom of selenium, the atomic weight of selenium can be calculated as follows:

$$\begin{aligned} \text{At. Wt. S.} & : \text{At. Wt. Se} = 18.39 : 45.40; \text{ or,} \\ 32 & : \text{At. Wt. Se} = 18.39 : 45.40. \end{aligned}$$

$$\text{At. Wt. Se} = \frac{32 \times 45.40}{18.39} = 79.$$

193. Molecular Formulae of Compounds. — It has already been shown how to find the simplest formula of a substance when its percentage composition by weight is known, but we have not been able to decide thus far whether the formula of acetylene, for example, is CH or $(\text{CH})_x$, where x is a whole number greater than unity. If the formula be CH, the molecular weight is 13. The molecular weight of acetylene is, however, approximately 26, so its formula must be C_2H_2 . In order to arrive at the formula of a gaseous compound, its density or molecular weight must be determined, as well as its percentage composition.

Example. — Acetylene and benzene are compounds having the same percentage composition, namely, carbon 92.3 and hydrogen 7.7. The relative density of acetylene is 13 (hydrogen = 1), while the relative density of the vapor of benzene is 39. Find the molecular weights and the formulae of the two substances.

(Atomic Weights : H = 1 (approximately), C = 12.)

	<i>Ratio of Atoms</i>
$92.3 \div 12 =$	7.7
$7.7 \div 1 =$	7.7
$7.7 : 7.7 =$	1 : 1.

CH is therefore the simplest formula.

Molecular weight = 2 *d* (187). For acetylene, the molecular weight is $2 \times 13 = 26$; therefore its formula is C_2H_2 . In the case of benzene, its molecular weight is $2 \times 39 = 78$. $78 \div 13 = 6$; therefore the formula of benzene is $(\text{CH})_6 = \text{C}_6\text{H}_6$. 26 g. of acetylene gas occupy 22.4 liters at S.T.P., while 78 g. of the vapor of benzene are required.

194. Molecular Weights and Formulae of Elementary Substances. — Molecules of elementary substances in the gaseous state contain from one to eight atoms.

In the following table, the first column contains the minimum weight of the element found in 22.4 liters of any compound, the

second column contains the symbol, which stands for this weight, the third column the molar weight, and the last column the molecular formula of the free substance.

Element	Gram-Atomic Weight	Symbol	Molar Weight, i.e., the Weight of 22.4 Liters	Formula of Free Element
Oxygen.....	16.00	O	32 = 16 × 2	O ₂
Ozone.....	16.00	O	48 = 16 × 3	O ₃
Hydrogen.....	1.008	H	2.016 = 1.008 × 2	H ₂
Nitrogen.....	14.008	N	28.016 = 14.008 × 2	N ₂
Chlorine.....	35.46	Cl	70.92 = 35.46 × 2	Cl ₂
Phosphorus....	31.03	P	124.12 = 31.03 × 4	P ₄
Sodium.....	23.00	Na	23 = 23 × 1	Na
Potassium.....	39.1	K	39.1 = 39.1 × 1	K
Zinc.....	65.38	Zn	65.38 = 65.38 × 1	Zn
Cadmium.....	112.4	Cd	112.4 = 112.4 × 1	Cd
Mercury.....	200.61	Hg	200.61 = 200.61 × 1	Hg
Sulfur (193°)...	32.06	S	256.48 = 32.06 × 8	S ₈
Sulfur (1,719°)...	32.06	S	64.12 = 32.06 × 2	S ₂

An examination of the table shows that some molecules are monatomic, i.e., the molecule is reduced to its lowest terms.

Monatomic molecules: Na, K, Zn, Cd, Hg, He, A, Ne, Kr, Xe, Ni, I (1,700°).

Diatomic molecules: O₂, H₂, N₂, Cl₂, Br₂, I₂ (448°), F₂, S₂ (1,719°).

Triatomic molecule: O₃.

Tetratomic molecules: P₄, As₄.

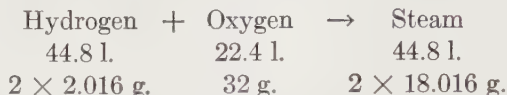
Octatomic molecule: S₈.

195. Molecular Equations. — Molecular equations should be used exclusively. To illustrate, let us make the molecular equation for the combination of hydrogen and oxygen. Two volumes of hydrogen combine with one volume of oxygen to form two volumes of steam:

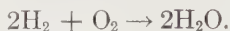


According to the law of Avogadro, the number of molecules of steam is equal to the number of hydrogen molecules, and double those of the oxygen. 22.4 liters of oxygen (32 g.) require 2×22.4 liters of hydrogen (2×2.016 g.) to form 2×22.4 liters of steam

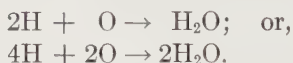
(2×18.016 g.), the volume being calculated to S.T.P. We may now write:



Now the only way to write the molecular equation to make it correspond with the facts is as follows:



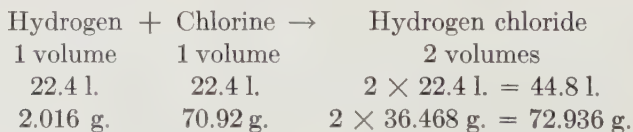
This shows that there are two molecules of hydrogen (and hence 2 volumes) for every molecule (1 volume) of oxygen and for every two molecules (2 volumes) of steam. Two molecules are formed from three, hence the volume is diminished by one-third. Show that the equation would not correspond with the facts if it were written thus:



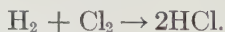
According to this equation, free hydrogen and oxygen are represented as being made up of monatomic molecules.

Review the relation of oxygen to ozone (116).

Again, when hydrogen and chlorine interact, hydrogen chloride is formed, and the volume of the product is equal to the sum of the volumes of the factors. This is another illustration of Gay-Lussac's law. Furthermore, it is found by experiment that 2.016 g. of hydrogen combine with 70.92 g. of chlorine to form 72.936 g. of hydrogen chloride. These facts may be expressed thus:



To make it harmonize with these facts, the equation must be written:



Show that the following equation is not in agreement with the above-mentioned facts:

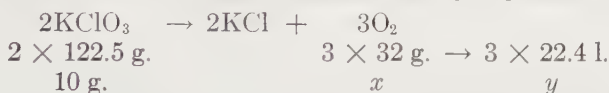


Note that the relative weights of a molecule of chlorine and of a molecule of hydrogen chloride stand to each other in the ratio of 70.92 : 36.468.

Inasmuch as a molecule of hydrogen chloride must contain at least one atom of chlorine, it accords with the facts to assume that its formula is HCl, while that of free chlorine, possessing a density of 70.92, must be Cl₂. It is evident that there cannot be a whole molecule of chlorine in a molecule of hydrogen chloride.

196. **Calculations Involving Molecular Equations.** — The volume of a gas in liters may be obtained by dividing the weight of the gas in grams by the weight of one liter of the gas. Calculations of volumes of gases may be much shortened by remembering that a mol of any gas occupies, at S.T.P., 22.4 liters (185). While this statement is only approximately true, it is accurate enough for ordinary purposes.

Example. — How much oxygen by weight and by volume, measured dry and at S.T.P., could be obtained by heating 10 g. of pure potassium chlorate?



By the equation we see that 245 g. of potassium chlorate yield 96 g. of oxygen which occupies 67.2 liters at S.T.P. The calculation can be made as follows:

(1) By Wt. 245 g. : 10 g. = 96 g. : x g., whence

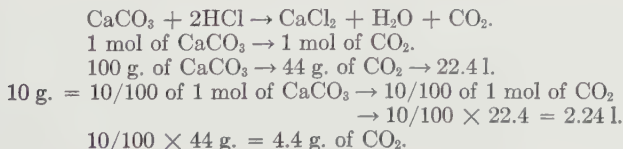
$$x = \frac{10 \times 96}{245} = 3.918 \text{ g. of oxygen.}$$

(2) By Vol. 245 : 10 = 67.2 l. : y l., whence

$$y = \frac{10 \times 67.2}{245} = 2.743 \text{ l. of oxygen.}$$

The following example illustrates an *alternative method* which some teachers prefer:

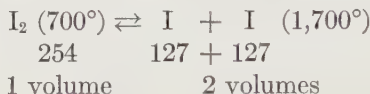
Example. — What weight and what volume (measured dry at S.T.P.) of carbon dioxide would be evolved by dissolving 10 g. of pure calcite (CaCO₃) in hydrochloric acid?



Apply this method to the solution of the following problem: How much oxygen by weight and by volume measured dry at S.T.P., could be obtained by the action of water upon 15.6 g. of pure sodium peroxide? What volume would the gas occupy at 20° and under a pressure of 775 mm. of mercury?

197. Dissociation and Molecular Weights. — Molecules of certain substances dissociate on heating into two or more molecules. As the number of gaseous molecules increases, the volume increases in the same ratio; but as the molecules are lighter, the density decreases. In other words, *substances which dissociate possess abnormal densities and molecular weights at higher temperatures.* Lowering the pressure likewise increases the dissociation. The following examples are good illustrations:

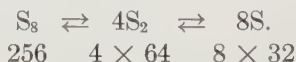
(1) Iodine vapor is diatomic (I_2) up to about 700°, but at 1,700° the molecule is monatomic and the molecular weight and density are reduced to one-half of their normal value:



(2) Phosphorus pentachloride also dissociates at higher temperatures, yielding phosphorus trichloride and chlorine. Above 300° the dissociation is practically complete:



(3) When sulfur is vaporized (B.P. 445°), its density varies with changes in temperature. At about 200° and under very low pressure, the molecule is octatomic (S_8); and at 800°, it is diatomic (S_2). Nernst found that 45 per cent of the diatomic molecules are dissociated at 1,900–2,000°:



When the vapor consists of octatomic molecules, the G.M.V. holds 256 g.; but at 800° the density is only one-fourth of the normal, so the G.M.V. holds only 64 g.

198. Calculation of the Degree of Dissociation. — The degree of dissociation may be calculated as follows: Let x = the degree of dissociation and 1 the molecular concentration. Let us assume that each molecule which dissociates yields two molecules; then $(1 - x)$ = the non-dissociated molecules, and $(1 - x) + 2x = (1 + x)$, the total number of molecules. But $(1 + x) = 1 + (2 - 1)x$. This expression may be made general by substituting n for 2, which gives $1 + (n - 1)x$. We have seen that the density

of a gas decreases as dissociation occurs. This means that the number of molecules of a given mass of a dissociating gas (or vapor, *e.g.*, I_2) is inversely as its density (or directly proportional to its volume); therefore we have —

$$1 : (1 + (n - 1)x) = d_{\text{observed}} : d_{\text{calculated}}; \text{ or,} \\ \frac{1}{(1 + (n - 1)x)} = \frac{d_{\text{obs.}}}{d_{\text{calc.}}}, \text{ whence } x = \frac{d_{\text{calc.}} - d_{\text{obs.}}}{d_{\text{obs.}}(n - 1)}$$

To illustrate: Victor Meyer found the vapor density of iodine to be 81.5 (hydrogen = 1) at $1,250^\circ$; calculate the degree of dissociation of iodine at this temperature. The molecular weights of gases may be taken as their densities; therefore the calculated mol. wt. of iodine vapor (I_2) is 254 (127×2). At $1,250^\circ$ the average mol. wt. of the vapor is 163 (81.5×2). Substituting in the formula, we have —

$$x = \frac{254 - 163}{163(2 - 1)} = 0.56 \text{ (approximately).}$$

This shows that at $1,250^\circ$ about 56 molecules of iodine vapor out of every hundred are dissociated.

EXERCISES

1. State Gay-Lussac's law of volumes and Avogadro's hypothesis (law) and show how the latter explains the former.

2. Show how Avogadro's law guides the chemist in the determination of the molecular weights of gases and vapors.

3. How is the gram-molecular volume arrived at?

4. 110 cc. of a gas, measured dry at 21° and 763 mm., weighed 0.1462 g. Find its molecular weight.

5. Explain the meaning of the following formulae, and show how they are derived:

(a) Mol. Wt. = 32 d.

(b) Mol. Wt. = 2 d.

(c) Mol. Wt. = 28.955 d.

6. A certain hydrocarbon compound contains 83.62 per cent of carbon. In a molecular weight determination by the Victor Meyer method, 0.120 g. of the substance displaced air which occupied 34.1 cc. when measured over mercury at 21° and 750 mm. Find the molecular weight of the compound.

7. The weight of a liter of a certain gas is 2.93 g., at S.T.P. What is its density referred to oxygen, and what is its molecular weight?

8. Three compounds were analyzed and found to contain the following percentages: carbon, 40.00; hydrogen, 6.67; oxygen, 53.33. One liter of the vapor of the first compound weighs 1.3393 g., at S.T.P., and the molar weight of the second is twice that of the first, and that of the third three times that of the second. Find the molecular formulae of the three compounds.

9. Tell concisely, yet fully, how you would determine the exact atomic weight of an element which forms a number of gaseous or volatile compounds.

10. State the law which may be employed for fixing the approximate atomic weight of an element of which no gaseous or volatile compounds are known, and show how the law may be applied.

11. A compound possesses the following composition: phosphorus, 20.23; oxygen, 10.43; chlorine, 69.34. Its vapor density referred to hydrogen is 77.95, and the specific heat of phosphorus is 0.202. Find the formula of the compound and the exact atomic weight of phosphorus. [Cl = 35.46, O = 16.]

12. A compound of uranium contains 10 g. of uranium to 2.0151 g. of oxygen. The specific heat of uranium is 0.0276. Find the equivalent weight of uranium, the formula of the compound, and the exact atomic weight of uranium. [O = 16.]

13. The vapor densities of three substances referred to hydrogen taken as unity were 16, 23, and 30 respectively, and the percentages by weight of one of their constituent elements (x) were 37.5, 52.18, and 60 respectively. From the data submitted, find the atomic weight of the element.

14. Two compounds have the following composition: carbon, 54.67 per cent; hydrogen, 9.11 per cent; oxygen, 36.22 per cent. The density of one of the compounds [oxygen = 1] is 1.375, and that of the other is 2.750. Find the molecular formula of each substance.

15. How much hydrogen by weight and by volume, measured over water at 22° and 748 mm., could be prepared by passing steam over 3 gram-atomic weights of pure iron? What would be the weight of the oxide?

16. What evidence is there for assuming that the molecules of hydrogen, oxygen, and chlorine are diatomic, the ozone molecule triatomic, and the sodium (vapor) molecule monatomic?

17. Explain the significance of "abnormal" vapor densities.

18. How can you show that water contains two separately replaceable portions of hydrogen? Of what interest is this historically?

19. If 49.33 g. of mannite, when dissolved in 1,000 g. of water, lower the freezing point 0.505° C., what is the molecular weight of the compound?

20. (a) The specific heat of gold is 0.033. Find its approximate atomic weight.

(b) 2.212 g. of an oxide of gold were decomposed by heat, and the metallic gold thus obtained weighed 1.972 g. Find the simplest formula of the oxide, the equivalent weight of gold, the valence of the metal, and its exact atomic weight. [O = 16.]

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CHAPTER XI

ENERGY AND CHEMICAL CHANGE. CHEMICAL EQUILIBRIUM

199. **Energy.** — The word energy is derived from the Greek, meaning “in work.” It is well known that when we wish to perform work on a large scale, we usually begin by the production of heat; therefore heat and work are very closely related, both being forms of energy. According to Ostwald, *energy is work and all else that can arise from work and be converted into work*. The work performed, therefore, is equal to the energy expended. Now, in performing work, heat, electricity, mechanical energy, etc., may be employed. These are different forms of energy.

200. **Potential and Kinetic Energy.** — Energy may be divided as follows:

Energy (The capability of doing work)	I. Potential Energy (Stored up Work, or Energy of Stress)	<ul style="list-style-type: none"> (1) Physical: <i>e.g.</i>, a coiled spring (2) Chemical: <i>e.g.</i>, energy in fuel and oxygen
	II. Kinetic Energy (Energy of Motion)	<ul style="list-style-type: none"> (1) Physical: <i>e.g.</i>, a body in motion (2) Chemical: <i>e.g.</i>, fuel in combustion

Potential Energy may be regarded as work stored up, or energy of stress. Thus, in our coal and oil deposits there are great stores of energy or possible work. Furthermore, a stone raised above the surface of the earth possesses potential energy. In falling, it can do work.

Kinetic Energy is the energy a body possesses by virtue of its motion: for example, a moving projectile, water in motion, the wind, and the combustion of fuel. When fuel undergoes oxidation, the molecules of the interacting substances rush together and break up to form new molecules at a high temperature. The view that heat is a form of kinetic energy is closely connected with the kinetic-molecular theory of matter.

The kinetic energy of a body of mass m moving with a speed

u is $1/2 mu^2$; that is, the kinetic energy of a body is one-half of its mass into the square of its speed (54).

201. **Transformation of Energy.** — The various forms of energy — heat, light, electricity, motion, etc., — may be converted into



Courtesy of the Westinghouse Co., East Pittsburgh, Pa.

FIG. 89. A 42-Foot Million-Volt Arc.

This arc illustrates the transformation of energy on a large scale, and rivals lightning in intensity.

each other (Fig. 89). Potential energy may be converted into kinetic energy, and *vice versa*. To illustrate, our coal supplies represent at present our largest available source of potential energy, being stored up sunshine of long geologic ages. When

coal is burned in the furnace of a steam boiler, potential (chemical) energy is transformed into kinetic energy in the form of heat, and the heat generates steam. In steam there is kinetic energy, due to the motion of the water molecules. As steam accumulates in the boiler, the pressure is increased, and the kinetic energy of the moving machinery is transformed into electricity, light, motion, the energy of chemical stress, and finally into heat again.

Moreover, solar energy reaches the earth in the form of heat, and heat evaporates water and the water forms clouds; rain falls, and water finds its way into rivers. When it reaches a precipice such as Niagara, it possesses a great deal of potential energy. In falling, the potential energy of the water is transformed into kinetic energy, which can set a wheel in motion (mechanical energy), the wheel in motion is capable of operating a dynamo, which generates electricity, which in turn may be transformed into light, heat, motion, etc.

202. The Conservation of Energy. — When we examine closely the various transformations of energy, we find that no body or system of bodies can acquire energy save at the expense of the energy possessed by another system. Man has never been able to create energy, neither has he been able to destroy it. In other words, "it is impossible to get something for nothing." It is clear, then, that perpetual motion is an impossibility. As experimenters have never observed any loss in the transformations of energy, a law has been formulated, known as the **Law of the Conservation of Energy**. It may be stated thus:

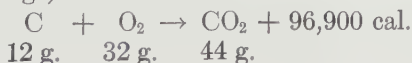
In a limited material system no gain or loss of energy is ever observed, though it may be transformed into any of the forms of which energy is susceptible.

This law is a fundamental law of physics, just as the law of the conservation of mass is a fundamental law of chemistry.

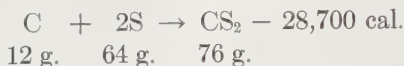
203. Energy and Chemical Change. — It may be stated, in general, that in every chemical action the formation of new substances is accompanied by a change in the energy of the system.

I. The production or consumption of heat may accompany a chemical change. Indeed, heat is the most common form of energy accompanying chemical change. The following are illustrations:

(1) When carbon burns, a great quantity of heat is liberated (exothermic change):



(2) When carbon and sulfur unite to form carbon disulfide, heat is consumed (endothermic change):



II. *Light may be produced or consumed.*

(1) When magnesium and phosphorus burn, intense light (also heat) is produced.

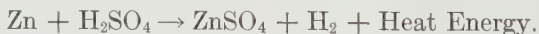
(2) Light is consumed in photography, being used up in changing the composition of silver salts. The effect of light on silver chloride may be observed by exposing freshly prepared AgCl (white) to sunlight; it turns bluish, then brown, as the decomposition into its constituents proceeds.

Photochemistry is now being studied industriously, and it is of great importance. Photochemical reactions are those which occur when a system is "illuminated." Both the light of the visible and ultraviolet spectrum have been employed, but there has recently developed a tendency to include all varieties of wave motion.

III. *Electrical Energy may be consumed or produced.*

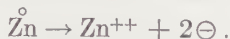
(1) It is consumed during the electrolysis of a substance: *e.g.*, when an electric current is passed through a solution of copper sulfate (CuSO_4), copper is deposited on the cathode. It is the function of the battery to supply the energy.

(2) When zinc is dissolved in diluted sulfuric acid, hydrogen and heat are liberated:



We have already seen that heat is the most common form of energy accompanying chemical change. It is possible, however, to carry out the interaction of zinc and sulfuric acid so as to make electricity appear instead of heat. This may be accomplished by immersing one end of a rod of zinc in sulfuric acid, and connecting the other end of the zinc by means of a copper wire to one of the binding posts of a galvanometer, the other post of which is connected with a piece of platinum foil, which is also immersed in sulfuric acid (Fig. 90). The needle of the galvanometer is deflected, showing that a current of electricity is produced. The source of the energy is the chemical energy stored in the interacting substances. The zinc atoms, which are electrically neutral,

in going into solution to form zinc ions (Zn^{++}), lose electrons:



The free electrons then pass through the rod of zinc, the wire, and the galvanometer, to the platinum electrode, and therefore constitute an electric current. Chemical energy is transformed into electrical energy. *In batteries, then, chemical energy is transformed into electrical energy instead of heat.* The energy of the current is known as the free energy of the reaction. In general, the free and total energies of a reaction are not equal.

IV. *Mechanical Energy may be produced or used up.*

(1) When trinitrotoluene (TNT) and dynamite explode, mechanical energy is produced. The chemical energy (potential) in the explosives is transformed into mechanical energy.

(2) By rubbing silver chloride vigorously in a mortar, mechanical energy is used up, as a result of which it is possible to liberate metallic silver and chlorine. Some of the energy, of course, appears as heat.

General Conclusion: A chemical reaction never occurs without some accompaniment of energy; heat is either produced or consumed, and other energy changes may occur.

204. **Importance of Energy in Chemistry.** — The energy changes which accompany many chemical changes are of very great importance. Thus, when a manufacturer buys fuel, he has its calorific value determined by the engineer. We burn fuel in order to transform chemical energy into mechanical energy with which we can carry on the useful work of the world. Electricity and light are also produced by certain chemical changes. Electricity may be stored in a battery, and as it runs down (chemical change), work may be performed, light produced, etc.

Matter and energy are associated, and as the former undergoes transformations it is of interest to study the energy changes.

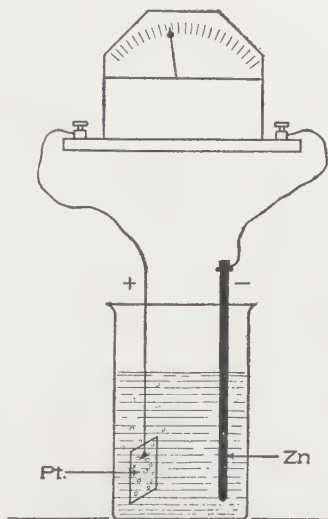


FIG. 90.

The energy stored up in coal, oil, gas, and other materials is sometimes called *internal energy*.

205. Energy and Chemical Activity. — Substances like phosphorus and oxygen are regarded as being “chemically active,” for they interact rapidly and there is a relatively large loss of internal energy. Carbon and oxygen are the greatest carriers of energy which is transformed into heat and work.

By the combustion of carbon, much internal energy is transformed into heat. Now, how may *relative chemical activity* be estimated?

(1) It may be estimated by observing the speed of chemical action, *i.e.*, the amount of matter undergoing chemical transformation in a suitable unit of time, say, a second or a minute.

(2) By measuring the quantity of heat accompanying the chemical change. This is done by means of a calorimeter (see Thermochemistry).

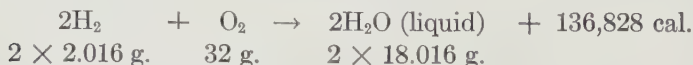
(3) By the electrical method. This is done by measuring the electromotive force of the current, the materials being arranged in the form of a battery-cell (203). The electrical method is the most convenient.

It should be understood that the chemical activity of a particular substance is not the same with respect to all other substances.

The methods outlined above are general, so in making comparisons by them the chemist must exercise care. Not only the affinities of the interacting substances must be considered, but also their concentrations.

206. Thermochemistry. — Thermochemistry is the branch of chemistry which takes account of the heat changes accompanying chemical reactions. Heat of combustion is determined in calories and is measured in an apparatus called a calorimeter.

Thermochemical equations give not only the mass (weight) relations of the various substances concerned in a chemical reaction, but also the heat produced or consumed:



This equation means that when 4.032 g. of hydrogen at 0° unite with 32 g. of oxygen, also at 0°, to form 36.032 g. of water at 0°, there is a sufficient quantity of heat liberated to raise the temperature of 136,828 g. of water one degree.

The heat of reaction depends, of course, upon the temperature

at which it is carried out, as well as upon the state of the substances involved. Thus, when the heat of reaction of water in the gaseous state is measured, it is less than that for liquid water, for steam gives out heat in condensing to liquid water.

Again, the equation,



means that 28 g. (1 mol) of nitrogen absorb 43,200 calories in combining with 32 g. of oxygen to form 60 g. (2 mols) of nitric oxide. This action is reversible, so when 60 g. of NO decompose, 43,200 calories are liberated.

Reactions in solution, *e.g.*, neutralization, are carried out in an ordinary open calorimeter, the heat evolved being imparted to a given mass of water surrounding the reaction vessel.

Heats of combustion, *e.g.*, of fuel, are measured by means of a **bomb calorimeter** (Fig. 91). It consists of a closed steel vessel lined with a refractory material such as platinum or enamel. Oxygen under pressure is admitted to the combustion chamber at *O*, and an electrically heated fuse-wire ignites the charge at *A*. The heat of combustion is imparted to a known mass of water in which the bomb is submerged. The water is stirred by a stirrer (*S*) and the increase in its temperature is noted by the thermometer *T*.

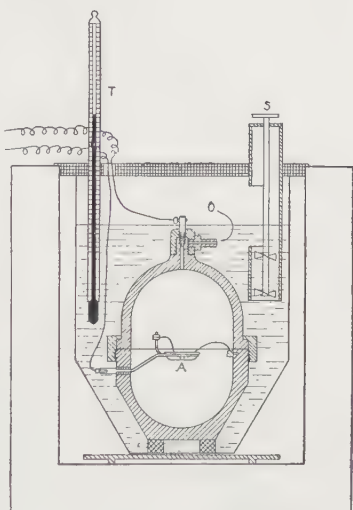


FIG. 91.

The method just described is a direct one for determining heat of reaction.

207. Thermochemical Laws. — There are two general laws which are applied constantly in the study of thermochemistry.

(1) The quantity of heat required to decompose a compound into its constituents is equal to the quantity evolved when the compound is formed from its elements.

Thus, 68,414 calories are required to decompose 1 gram-molecular weight of water.

The *heat of formation* of a substance is the quantity of heat evolved or absorbed in the formation of a gram-molecular weight from its elements.

This law was first formulated by Lavoisier and Laplace.

(2) **The Law of Constant Heat Summation:**

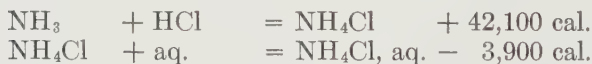
When a chemical compound is formed, the heat of formation is the same whether the compound be formed directly or by several successive steps.

This law was formulated by the chemist, G. H. Hess, of St. Petersburg, in 1840.

It is therefore possible to determine heat of reaction indirectly. The law is a corollary of the more fundamental law of the conservation of energy.

To illustrate the law, let us consider the heat of formation of ammonium chloride, which may be formed either by allowing gaseous ammonia and hydrogen chloride to interact and then dissolving the product in water; or by first dissolving separately each of the gases in water and then mixing the solutions. The symbol aq. used below is from Latin *aqua*, water.

First Way



Total heat produced : 38,200 cal.

Second Way

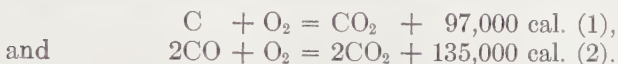


Total heat produced : 38,000 cal.

These figures show that the total heat liberated in the two cases is the same within the limits of experimental error. The heat developed therefore in a chemical change depends only on the initial and final stages of the system and is independent of the intermediate stages through which the system passes.

It follows that thermochemical equations may be treated as algebraic equations; that is, they may be added or subtracted.

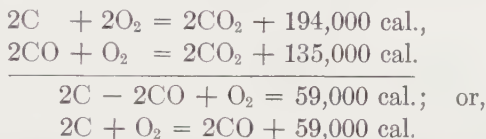
Example: the following heats of reaction are true:



Find the heat of reaction of



By multiplying equation (1) by 2 and then subtracting equation (2) from it, we have:



This heat of reaction is thus found by the indirect method. The heat of reaction for CO_2 may be measured in a calorimeter by the direct method.

The development of thermochemistry has been largely due to the labors of Julius Thomsen, of Copenhagen, and M. Berthelot, of Paris, and their pupils. The former chemist began work in 1853 and the latter in 1873. The two principles or laws stated above constitute the bases of thermochemistry.

It is interesting to note that very little was known about energy a century ago. The great modern development of civilization is due very largely to the utilization of energy. Our age may be truly called the Age of Energy, or the Age of Steam and Electricity. Man has acquired gradually a mastery over matter, or the material world.

It should be clearly kept before us that the application of energy is closely connected with the wealth and prosperity of a nation; and it is fortunate that one nation after another has taken intelligent steps for the conservation of natural resources. The necessity of conservation was brought home to us particularly during the recent war.

208. Bioluminescence: "Cold Light." — Certain forms of life, such as the firefly, the glowworm, and some of the small creatures of the sea, are able to produce light without any appreciable accompaniment of heat. These forms of life are said to luminesce. **Luminescence**, as used in this connection, is therefore a light which is produced at a comparatively low temperature — "cold light."

At least forty orders of animals contain one or more light-producing forms, and two groups of plants — fungi and bacteria — are luminescent. The luminescence of damp wood ("fox-fire")

is due to a fungus in the wood, and it is well known that dead fish or meat may glow in the dark, due to bacteria.

Fungi and bacteria produce light continuously, while the various forms of animal life produce light only when stimulated in some way: *e.g.*, the "phosphorescence" produced in a heavy sea, or when the water is churned up by the propeller of a boat. The higher forms of animal life, such as the firefly, can turn on their lights without external stimulation.

Bioluminescence ("phosphorescence") has nothing to do with phosphorus.

Luminescent animals are efficient, for they are able to produce light without the loss of appreciable energy in the form of heat.

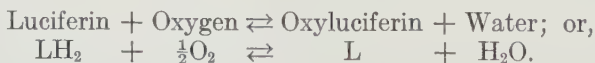
As stated by E. N. Harvey, *our chemical knowledge of luminescence has advanced in four important steps*:

(1) R. Boyle (1667) placed a small piece of luminescent wood in an air-pump and found that it ceased to glow when the air was removed, and reappeared when air was admitted again. *Luminescence therefore occurs in the presence of oxygen.*

(2) L. Spallanzani, an Italian, discovered (1794) that *all luminescence requires water*. When luminescent tissue is dried rapidly, it can be preserved for a long time; but when water is added, the light reappears.

(3) The Frenchman, R. Dubois (1865), showed that two substances (in addition to oxygen and water) are necessary in the production of luminescence — *luciferin* and *luciferase*. The exact composition of these substances is not known. The former is oxidized in the animal (or plant), and the latter is a catalytic enzyme which induces oxidation.

(4) Finally, Harvey has arrived at the conclusion that luciferin is oxidized to what is termed oxyluciferin (see Oxyhemoglobin) which is then reduced to luciferin. When the firefly flashes its light, oxyluciferin is produced; but between flashes oxyluciferin is reduced to luciferin. The reaction is reversible, being essentially as follows:



Note that this is a very economical process, for the animal first burns an "oil," which is re-formed between flashes, ready to be re-burned.

Harvey mimics animal luminescence by the following *experiment*:

"If one takes, for instance, a test-tube containing a minute quantity of pyrogallie acid solution, with a little hydrogen peroxide added, and to that test-tube adds potato juice, one gets a luminescence. The potato juice supplies an enzyme that acts as the luciferase does in luminous animals. Pyrogallie acid corresponds to luciferin." The peroxide furnishes oxygen to oxidize pyrogallie acid.

It is too early as yet to determine whether it will ever be possible to produce "cold light" on a commercial scale.

Luciferin and luciferase can be prepared and experimented with like any other chemical substances, but their exact structure is not yet known. Luciferin appears to be one of the simpler members of the proteins, such as the peptones or proteoses; while luciferase is related to the albumins. In case chemists should succeed in synthesizing proteins and discovering the structure of their molecules, it is quite likely that they would be able to produce the substances concerned in the production of luminescence, and this would perhaps lead to heatless illumination. Ceilings might be painted with the luminescent material, and when darkness fell the paint would begin to glow. By increasing or decreasing the painted area, the light could be made stronger or weaker. Just as different organisms give off light of different colors, different lights might be produced by artificial means; and the light could be regulated by means of screens or coverings. When the chemist can write the structural formula — *i.e.*, the arrangement of the atoms in the molecule — of the photogenic substance found in the cells of living organisms and explain exactly how its oxidation is produced, the problem of light-production by living creatures will be solved.

CHEMICAL EQUILIBRIUM

209. Irreversible Reactions. — Many chemical reactions may be carried to completion, or practically so. Thus, when potassium chlorate is heated, it decomposes into potassium chloride and oxygen. The reverse action, namely, the combination of the products to form potassium chlorate, has never been accomplished. The reaction is, therefore, irreversible:



Again, when magnesium is burned in oxygen magnesium oxide is formed, which does not dissociate appreciably into its elements, even at a very high temperature. A given mass of metal may be

completely oxidized by burning it in a sufficient supply of oxygen. As is well known, magnesia is employed as a lining for crucibles and furnaces. Lime (CaO) is another exceedingly stable oxide (the Drummond light).

210. Reversible or Opposing Reactions. — Chemists have learned by experiment that by choosing suitable conditions a great majority of chemical actions may be made to proceed in either direction. According to H. S. Taylor, "there is no reason to believe that any reaction is not reversible, at least for the purpose of theoretical considerations." We have seen that mercury and oxygen may be obtained by heating mercuric oxide; also, that mercury and oxygen unite under certain conditions to form mercuric oxide (95). This reaction is, therefore, reversible:



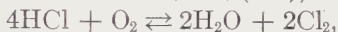
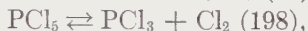
Again, when hydrogen is passed over hot magnetic oxide of iron, the oxide is reduced to metallic iron; also, hydrogen can be formed by reducing steam with hot iron (125):



In order to complete the forward action, an excess of hydrogen must be employed and the water removed. This may be accomplished by condensing the steam. By passing an excess of steam over hot iron and removing the hydrogen, the action to the left may be completed. If iron oxide and hydrogen were heated together in a closed vessel, say at 440° , a chemical equilibrium would be established between the substances on the left of the equation and those on the right. This condition of apparent rest or equilibrium is reached when the speed of the action to the right is just balanced by the speed of the action in the reverse direction. Equilibrium also would be established by starting with the pair of substances — iron and steam. If we start by heating iron oxide and hydrogen together, the speed of the forward action begins at a maximum, while the speed of the reverse action starts at zero. The speed of the forward action becomes slower and slower, and that of the reverse action faster and faster until the two speeds are equal. At equilibrium there is no further change in the concentrations of the reacting substances. It should be borne in mind, however, that we have not a state of repose, but a balanced action. Experiment shows that at 440° equilibrium is established when the volume of the steam is to the

volume of hydrogen nearly as 6 : 1. This means that if 6 volumes of steam and 1 volume of hydrogen be passed over iron oxide or iron at 440°, no apparent change will take place; for the gaseous mixture will have the same composition after passing through the tube as it had upon entering it.

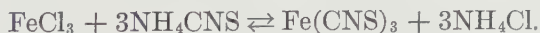
Other common reversible actions are as follows:



We see, therefore, that there are incomplete chemical reactions, just as there are incomplete physical processes (re-read 144).

211. The Effect of Concentration. — The speed of a chemical change at a given temperature depends upon the number of encounters between the molecules of the interacting substances, as well as upon their intrinsic affinity or activity. Reactions between concentrated solutions occur with greater speed than do those between dilute solutions, because the molecules encounter each other more frequently. It is the concentration of the molecules which is effective, and not the mere addition of a greater quantity of a certain reagent. To illustrate, hydrogen is not liberated more rapidly by treating a small piece of zinc with a large quantity of dilute sulfuric acid than it is by using a smaller quantity; but 10 cc. of 5 *N* acid will interact more rapidly with a given mass of zinc than will 10 cc. of a more dilute acid, say, 2 *N*. In the case of the more concentrated acid, a larger number of molecules of sulfuric acid come into contact with the zinc in a unit of time.

The influence of concentration on a system in chemical equilibrium may be illustrated by a reaction studied by J. H. Gladstone in 1855. When a very dilute solution of ferric chloride, FeCl_3 , is treated with a dilute solution of ammonium thiocyanate, NH_4CNS , a blood-red solution is obtained, due to the formation of ferric thiocyanate, $\text{Fe}(\text{CNS})_3$. The reaction is reversible:



All the compounds involved are quite soluble in water, giving a homogeneous mixture.

A reddish solution of suitable concentration for the experiment may be prepared by adding 20 cc. of a decinormal solution of ferric chloride to 2 liters of water, followed by the addition of 20 cc. of a decinormal solution of ammonium thiocyanate, which is the amount of the latter required to interact with the former according to the equation. Equal volumes of the reddish solution are now poured into four test-glasses or beakers, and one of the solutions kept for reference. When a few drops of a concentrated solution of ferric chloride are added to one of the solutions, the color deepens, for the forward change is accelerated; that is, there is a shift in the equilibrium to the right. Likewise, when a few drops of a concentrated solution of ammonium thiocyanate are added to another portion of the solution, the color deepens on account of the formation of more ferric thiocyanate. When the remaining portion of the liquid is treated with a few drops of a concentrated solution of ammonium chloride, the reddish color partially fades, or the equilibrium is shifted to the left. This shows that when the concentration of ammonium chloride is increased, the molecules of the substances on the right-hand side of the equation encounter each other more frequently in a given period of time; consequently they interact to form more of the substances on the left. At equilibrium, all four compounds exist in solution, and their concentrations are definite. Changing the concentration of either of the interacting substances on the same side of an equation causes a displacement of the equilibrium so as to form more of the substances on the other side.

212. The Law of Mass Action. — This very important law was formulated in 1867 by Guldberg and Waage of Christiania. The law may be stated thus:

The speed of chemical action is proportional to the "active mass" (or molecular concentration) of each of the reacting substances.

It should be noted that the French chemist C. L. Berthollet, about the beginning of the nineteenth century, realized that chemical action is conditioned not only by the affinities of the interacting substances, but by their relative masses. Guldberg and Waage revived and developed Berthollet's doctrines.

The idea of a dynamic equilibrium rather than a static, in opposing reactions, was emphasized by Williamson about the middle of the last century.

213. Speed of Chemical Change. — The speed of chemical change, or the rate of a chemical reaction, means the amount of

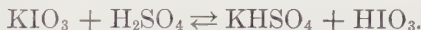
chemical transformation per unit of time, and is measured by determining the mols transformed per unit of time.

The *speed of chemical action* may be illustrated by the following *experiment*:

(1) Prepare a solution of potassium iodate, KIO_3 , by dissolving 2 g. of the substance in a liter of water. We may designate it as solution (A).

(2) Dissolve 0.4 g. of sodium bisulfite, NaHSO_3 , in 900 cc. of freshly-boiled water, add 5 cc. of molar sulfuric acid, and then 100 cc. of a starch solution (suspension) prepared by rubbing about 2 g. of starch with a little cold water to a paste, and then adding 100 cc. of water, followed by heating to boiling. The starch solution is allowed to cool before adding it to the solution of sodium bisulfite and sulfuric acid. The solution thus prepared will be designated as solution (B). It is essentially a solution of sulfurous acid.

When solutions (A) and (B) are mixed, iodic acid, HIO_3 , is formed:



Solution (A) is, therefore, essentially a solution of iodic acid.

Mix equal volumes, say, 100 cc., of solutions A and B and measure by a stop-watch the exact time required for the solution suddenly to turn blue. By varying the concentrations and the temperatures of the solutions, the time will be found to change. The experiment is often called the “**iodine clock**.” The explanation of this experiment is based upon consecutive reactions:



The solutions are so prepared that HIO_3 is present in excess. Reaction (1) is not as rapid as reaction (2), but reaction (3) is very much faster. The result is that so long as H_2SO_3 is present, iodine cannot be detected, because it is used up in reaction (3) as quickly as it is formed. As soon, however, as all the H_2SO_3 is consumed, reaction (3) necessarily stops, and the iodine set free in reaction (2), which keeps on going, instantaneously colors the starch.

214. Formulation of the Law of Mass Action. — Let us assume that substances A and B interact to form substances C and D:



The speed (S_1) of the reaction at any given time, from left to right, is

$$S_1 = [A] \times [B] \times K_1 \quad (2)$$

where $[A]$ and $[B]$ represent the active masses of A and B present at the time and K_1 their intrinsic affinity. If the reaction is reversible, the speed of the opposing reaction is represented by the expression

$$S_2 = [C] \times [D] \times K_2 \quad (3)$$

At equilibrium, $S_1 = S_2$; therefore,

$$[C] \times [D] \times K_2 = [A] \times [B] \times K_1, \quad \text{whence}$$

$$\frac{[C] \times [D]}{[A] \times [B]} = \frac{K_1}{K_2} = K \quad (4)$$

K is called the **Equilibrium Constant**.

In equations in which there is more than one molecule of a substance, the molecular concentration is raised to the power indicated by the number of molecules of the particular substance in the molecular equation. Thus, when steam is passed over hot iron, we have:



At equilibrium, the expression is

$$\frac{[\text{Fe}_3\text{O}_4] \times [\text{H}_2]^4}{[\text{Fe}]^3 \times [\text{H}_2\text{O}]^4} = K.$$

Guldberg and Waage were aware of the difficulty introduced by the use of the term "active mass," and pointed out that apparently "molecular concentration" can be employed instead in the cases of dissolved and gaseous substances. The active mass of a solid may be considered to be constant.

215. Law of Mass Action and the System — Hydrogen, Iodine, and Hydrogen Iodide. — When hydrogen iodide (HI) is heated in a closed glass tube to 445° (B. P. of sulfur), equilibrium is established when the percentage of hydrogen iodide reaches 79 and that of the iodine and hydrogen is 21:



Approximately, from every 100 molecules of HI, we obtain 10 molecules of H_2 and 10 of I_2 , and have 80 molecules of HI left.

Prolonged heating has no apparent effect on this system, which is now in equilibrium.

The speed of the forward action depends upon the molecular concentration of the hydrogen iodide and upon its intrinsic affinity. Representing these by S_1 , $[HI]$, and K_1 , respectively, we have:

$$S_1 = [HI] \times [HI] \times K_1 = [HI]^2 \times K_1.$$

The concentration of the hydrogen iodide is squared, because the molecule appears twice in the equation. Similarly, for the reverse action, we have:

$$S_2 = [H_2] \times [I_2] \times K_2.$$

At equilibrium, $S_1 = S_2$; therefore,

$$\begin{aligned} [HI]^2 \times K_1 &= [H_2] \times [I_2] \times K_2, \text{ or} \\ \frac{[H_2] \times [I_2]}{[HI]^2} &= \frac{K_1}{K_2} = K, \text{ the Equilibrium Constant.} \end{aligned}$$

Stated in words, this algebraic equation means that for the condition of equilibrium at a given temperature the product of the numbers of mols of hydrogen and of iodine per liter, divided by the square of the number of mols per liter of hydrogen iodide, is a constant quantity.

Example. — At 445° , we have about 80 per cent of HI and 20 per cent of H_2 and I_2 , or the ratio is 0.8 to 0.2. In every 100 molecules there are 80 of HI, 10 of H_2 and 10 of I_2 . The concentrations are, therefore, 0.8, 0.1, and 0.1 respectively. Substituting these values in the formula as deduced above, we have:

$$\frac{(0.1 \times 0.1)}{0.8^2} = \frac{0.1^2}{0.8^2} = \frac{1}{64}, \text{ the Equilibrium Constant.}$$

This means that hydrogen and iodine would unite with 64 times as great a speed as hydrogen iodide would dissociate if each reaction could be carried out without reversal and under the same conditions, say, when the concentrations of the gases are unity, the temperature being 445° .

216. Displacement of Equilibria. — Chemical equilibria may be displaced by different means:

(1) *By changing the concentration of one of the substances involved in the action.* Thus, in the preparation of hydrogen chloride (292), the equilibrium can be displaced forward by increasing the concentration of sulfuric acid. Displacing equilibria by change of

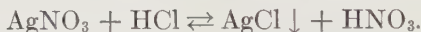
concentration is not very effective in many cases. In general, it is necessary to have a large excess of one of the substances, so this method is not as effective as some others.

(2) *By restraining or annulling the reverse action.* In case one of the products of a chemical action is a slightly soluble gas or an insoluble solid (precipitate), while the others are solids or solutions, the action has a tendency to run to completion. For example, when a mixture of common salt and sulfuric acid is heated, hydrochloric acid gas is expelled, and thus removed from the sphere of action. Again, quicklime (CaO) is manufactured by heating limestone (CaCO₃) in kilns:



The gaseous product, CO₂, is removed or allowed to escape, so the action has a tendency to run to completion.

When solutions of silver nitrate and of hydrochloric acid are mixed, silver chloride, a very slightly soluble compound, is formed:



A quantitative yield of silver chloride can be obtained by treating a solution of a silver salt with an excess of hydrochloric acid; that is, no appreciable amount of silver salt is left in solution.

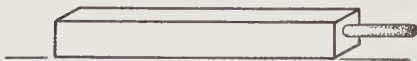


FIG. 92.

Equilibria may be displaced effectively by converting a substance from the gaseous to the liquid or solid phase. Thus, one end of a glass tube containing HI, H₂, and I₂ in equilibrium (Fig. 92), say, at 445°, might be cooled, whereby the iodine would be condensed to a solid, which would bring about the dissociation of more HI:



In general, if the products of a chemical action separate into a heterogeneous mixture, the reverse action is either restrained or virtually annulled. In carrying out chemical actions in the laboratory, as well as in manufacturing processes, reversibility is avoided, if possible.

217. Influence of Temperature on Chemical Actions. — The speed of practically all chemical changes is remarkably hastened by increase in temperature. *Roughly speaking, the speed is*

doubled when the temperature is raised 10°. It can be readily calculated from this statement that the speed of a reaction is increased more than 1,000 times by raising the temperature by 100°, and more than 1,000,000 times by raising the temperature by 200°. Hence the importance of burners and furnaces in carrying out experimental work and in manufacturing. In a reversible action, the relative amounts of the products and factors are changed when the temperature is altered; that is, by changing the temperature the equilibrium is displaced. Thus, when sulfur dioxide and oxygen interact to form sulfur trioxide, heat is liberated:



The reaction is strongly exothermic.

The following percentages of SO_2 are oxidized to SO_3 at equilibrium: at 400°, 89; at 550°, 85; at 645°, 60; and at 900°, practically none. The reverse change, $2\text{SO}_3 \rightarrow 2\text{SO}_2 + \text{O}_2$, is therefore favored by rise of temperature.

Again, when phosphorus pentachloride is heated, it dissociates with absorption of heat (endothermic reaction):



At 200° and 760 mm., 51.5 per cent of PCl_5 is present; but at 300°, only 3 per cent of the pentachloride is present. As the reaction is endothermic, rise of temperature displaces the equilibrium forward.

218. Law of Mobile Equilibrium. — The reactions just discussed are illustrations of a general principle known as **van't Hoff's Law of Mobile Equilibrium**, which may be stated thus.

If we heat a system in equilibrium, the equilibrium is displaced in the direction which consumes heat.

Thus, the dissociation of phosphorus pentachloride is favored by increase of temperature, for heat is absorbed.

van't Hoff's law is a special case of a more general principle known as **Le Chatelier's Law**:

If we bring some stress or force to bear upon a system in equilibrium, the equilibrium is displaced in a direction which tends to diminish the intensity of the stress or force.

Thus, when we evaporate a liquid by the application of heat, the latter is absorbed by the evaporating liquid. This means that as a liquid evaporates, the temperature tends to fall. Making

use of Le Chatelier's law, explain why ice melts when subjected to pressure.

EXERCISES

1. Define, and also illustrate, the following terms: (1) energy, (2) work, (3) potential energy, (4) kinetic energy, (5) internal energy.

2. Explain thoroughly what is meant by the transformation of energy. What is the original form of energy in (1) a steam-engine, (2) an automobile, (3) a waterfall, (4) a projectile in motion, (5) a watch?

3. Describe a simple battery-cell. Explain the source of the current.

4. State the law of the conservation of energy. Why is perpetual motion an impossibility?

5. Describe some chemical changes in which the following forms of energy are produced and consumed: (1) heat, (2) light, (3) electricity, (4) mechanical energy.

6. Define thermochemistry. What is the difference between temperature and quantity of heat? Define the unit of heat. How is quantity of heat measured?

7. Outline methods for measuring relative chemical activity.

8. Write an equation to show an exothermic reaction and an endothermic one. Point out the full significance of these equations.

9. Calculate the heat of formation of a mol of each of the following substances: (1) water (vapor), (2) carbon dioxide, (3) sulfur dioxide, (4) copper oxide, (5) magnesium oxide (see Appendix). How much heat would be required to dissociate a mol of water?

10. Suggest a method for the determination of the heat value of foods. What is the relation of the fuel value of foods to the heat of the body and muscular activity?

11. State, explain, and illustrate two laws of thermochemistry.

12. State the steps by means of which our knowledge of animal luminescence has been advanced.

13. Write molecular equations for several reversible chemical reactions and show how the equilibria may be displaced backward and forward.

14. Describe experiments to show the influence of concentration and of temperature upon the speed of chemical action.

✓ 15. State the law of molecular concentration (mass action). From the general equilibrium reaction represented by the equation, $A + B + \dots \rightleftharpoons C + D + \dots$, show how the following algebraic equation may be derived, and explain its meaning:

$$\frac{[C] \times [D] \cdot \cdot \cdot}{[A] \times [B] \cdot \cdot \cdot} = K.$$

✓ 16. Outline the chemistry of the "iodine clock."

17. Write down a concentration equation showing the equilibrium of iron with steam. Iron and iron oxide are solids; do the amounts of these substances have any influence on the chemical equilibrium? Upon what will the equilibrium in this system finally depend?

18. In any equilibrium reaction, *e.g.*, in the one represented by the equation $3\text{Fe} + 4\text{H}_2\text{O} \rightleftharpoons \text{Fe}_3\text{O}_4 + 4\text{H}_2$, would it make any difference in the final equilibrium which set of substances one starts with?

19. State how you would bring to completion (1) the dissociation of mercuric oxide; (2) the reduction of magnetic oxide of iron by means of hydrogen; (3) the synthesis of hydrogen iodide from hydrogen and iodine; (4) the conversion of copper sulfate into copper sulfide; and (5) the conversion of calcium carbonate into quicklime.

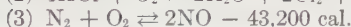
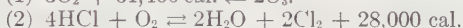
20. At equilibrium, experiment showed that there were in a liter 3 mols of SO_2 , 1 mol of O_2 , and 2 mols of SO_3 . Find the equilibrium constant, K .

Note. — $2\text{SO}_3 \rightleftharpoons 2\text{SO}_2 + \text{O}_2$. *Ans.*, 2.25.

21. If 5 mols of O_2 and 2 mols of SO_3 are in equilibrium with SO_2 , find the molecular concentration of SO_2 . *Ans.*, 1.34.

Note. — $\frac{[\text{SO}_2]^2 \times [\text{O}_2]}{[\text{SO}_3]^2} = 2.25$. Find the value of $[\text{SO}_2]^2$, from which the value of $[\text{SO}_2]$ may be readily found.

22. In case of the chemical reactions represented by the following equations, show the effect of rise of temperature upon the equilibrium point:



Would a medium temperature or a very high temperature favor the production of NO from its elements?

When chlorine is manufactured by Deacon's process (271), explain why the yield is greater at 370° than at 450° .

23. State the principle upon which is based the statement that endothermic substances are more stable at high temperatures. Illustrate by means of examples. Would it be logical to assume that all compounds are dissociated into their elements at the temperatures which prevail in certain stars ($15,000^\circ$ – $25,000^\circ$)?

24. (1) Making use of Le Chatelier's principle, explain the effect of increase of pressure upon the melting point of ice.

(2) If a substance dissolves in water with evolution of heat, state whether or not you would expect it to be more soluble at higher than at lower temperatures. Explain.

(3) Explain the effect of pressure in the synthesis of ammonia:



READINGS AND REFERENCES

FOSTER. The Romance of Chemistry, Chap. VI.

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HILDEBRAND. Principles of Chemistry, Chaps. IX, XI–XIV.

OSTWALD. Principles of Inorganic Chemistry, Chap. I.

PARTINGTON. Inorganic Chemistry, Chap. XX.

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CHAPTER XII

THE THEORY OF IONIZATION

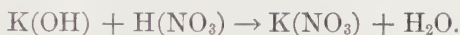
219. Introduction. — In our study of the influence of the solute upon the solvent (176), it was stated that aqueous solutions of the three classes of compounds known as acids, bases, and salts do not behave in the regular or normal way. To illustrate: A dilute solution of cane sugar has a normal freezing point, boiling point, and osmotic pressure, while a solution of sulfuric acid, sodium hydroxide, or sodium chloride of a concentration identical with that of the sugar solution has a lower freezing point, a higher boiling point, and higher osmotic pressure. Furthermore, the sugar solution is a non-conductor of electricity, while the other solutions are conductors, *i.e.*, they are electrolytes. In order to account for the different behavior of electrolytes we shall endeavor to prove that the molecules of acids, bases, and salts, in the presence of water, are more or less dissociated into particles and that these particles are the radicals — simple or complex — which constitute the molecules. The evidence of molecular dissociation will be considered under the following heads:

- (I) The Chemical Department of Acids, Bases, and Salts.
- (II) The Freezing Points of Solutions.
- (III) The Boiling Points of Solutions.
- (IV) The Osmotic Pressures of Solutions.
- (V) The Electrical Conductivity of Electrolytes.

220. Properties of Acids, Bases, and Salts. — It has already been pointed out that all acids contain hydrogen which may be displaced by magnesium and other metals, and that their aqueous solutions possess a sour taste and turn blue litmus red. An acid always gives the same reaction independently of the nature of the other constituent or constituents of the compound; that is, it contains hydrogen which behaves in a manner essentially different from the hydrogen in such compounds as sugar, alcohol, and hydrocarbons.

It was also pointed out that bases are hydroxides of metals,

that their aqueous solutions possess a soapy taste and turn red litmus blue. The hydroxyl radical (OH) is present in all bases: *e.g.*, sodium hydroxide, Na(OH); calcium hydroxide, Ca(OH)₂. Bases, like acids, contain two radicals. Salts also contain two radicals, a positive or metallic radical and a negative or acid radical: *e.g.*, silver nitrate, AgNO₃, contains the silver radical (Ag) and the nitrate radical (NO₃). Salts are readily formed by mixing a solution of a base with an acid, the chemical change being known as neutralization:

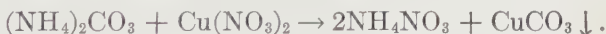


The compounds on the left-hand side of the equation exchange radicals instantaneously to form a salt and water. This reaction is characteristic of all bases and acids. Solutions of all bases appear to contain a common radical (OH), and those of acids contain the hydrogen radical.

Moreover, solutions of salts interact by double decomposition to form other salts. Thus, when a solution of silver nitrate is treated with one of sodium chloride, silver chloride is formed at once:



Likewise, when a solution of ammonium carbonate is treated with one of cupric nitrate, a precipitate is formed. The equation for the reaction is essentially as follows:



Note that the action takes place at once and without the necessity of heating the substances. Let us contrast with this reaction the one which occurs by heating together in a test-tube dry, solid ammonium carbonate and partially dehydrated cupric nitrate (solid). The reaction takes place slowly at first and becomes more vigorous as the temperature is raised, finally producing a great cloud of gas and smoke. Many different products are formed, such as ammonia (NH₃), carbon dioxide (CO₂), nitrous oxide (N₂O), nitrogen peroxide (NO₂), and cupric oxide (CuO). In short, this reaction which occurs in the absence of the solvent water is very complicated, and heat is required; but when solutions of the salts are mixed, the radicals of the factors exchange in a perfectly definite way to form other salts (products).

To sum up, the chemical behavior of aqueous solutions of acids, bases, and salts leads us to believe that their molecules, in the

presence of the solvent water, are dissociated into radicals, which exchange places very simply and readily when solutions are mixed.

221. Freezing Points of Solutions. — We have seen that equal numbers of molecules of different solutes in the same quantity of solvent produce equal depressions of the freezing point (177). Now, gram-molecules (mols) of different substances contain the same number of molecules. The table below shows the depression of the freezing point of water for several different solutions of equal concentration.

DEPRESSION OF THE FREEZING POINT OF WATER

Substance	Formula	Character	Depression Produced by 1 Mol of Substance in 1,000 g. of Water
Alcohol.....	C_2H_6O	non-electrolyte	1.85°
Dextrose (Glucose) ..	$C_6H_{12}O_6$	non-electrolyte	1.87°
Glycerine.....	$C_3H_8O_3$	non-electrolyte	1.86°
Hydrogen chloride...	HCl	acid (electrolyte)	3.81°
Hydrogen nitrate....	HNO_3	acid (electrolyte)	3.80°
Sodium hydroxide....	$NaOH$	base (electrolyte)	3.47°
Potassium hydroxide.	KOH	base (electrolyte)	3.77°
Potassium chloride...	KCl	salt (electrolyte)	3.29°
Sodium nitrate.....	$NaNO_3$	salt (electrolyte)	3.15°

This table shows that 1 mol of a non-electrolyte, such as a sugar or glycerine, dissolved in 1,000 g. of water, lowers the freezing point about 1.86° . This is known as the *molecular depression constant for water*. A mol of an acid, base, or salt, however, when dissolved in 1,000 g. of water, has an abnormally low freezing point. The only satisfactory explanation of this fact is to assume that molecules of these three classes of compounds dissociate into particles of less mass, or radicals, thus yielding a larger number of particles. To illustrate, we may assume that a molecule of potassium chloride dissociates thus:



The depression of the freezing point is proportional to the number of particles. In this particular case two particles are formed from one molecule of the salt.

It is clear from what has been said that a mol of calcium chloride would be much more effective in lowering the freezing point of a given mass of water than would be a mol of alcohol.

222. The Boiling Points of Solutions. — It has been shown that a mol of such a substance as sugar, when dissolved in 1,000 g.

of water, raises the boiling point approximately 0.52° . This is regarded as the normal elevation of the boiling point when water is the solvent. But when 1 mol of sodium chloride (58.5 g.) is dissolved in 1,000 g. of water, the solution boils at 100.87° . This shows that the elevation of the boiling point is abnormally high, or the vapor pressure of the solution is abnormally low. In general, solutions of acids, bases, and salts (electrolytes) have abnormal boiling points and vapor pressures, while solutions of non-electrolytes, *e.g.*, the sugars, have normal.

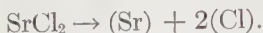
This difference in physical properties of the two classes of substances is readily accounted for by assuming that molecules of acids, bases, and salts dissociate in the presence of water, thus yielding a larger number of particles.

The boiling point of a solution depends upon the number of molecules or particles in solution, being independent of their nature.

223. The Osmotic Pressure of Solutions. — The osmotic pressure of dilute solutions is proportional to the concentration (mols per liter); also, the osmotic pressure exhibited by a substance (*e.g.*, sugar) in a dilute solution is somewhat analogous to the gaseous pressure the substance would exert if it existed as a gas at the same temperature and were confined in the same volume. To illustrate: If 1 mol (32 g.) of oxygen were confined at 0° in a space of 22.4 liters, it would exert a pressure of 1 atmosphere; or, if the oxygen were forced into a space of 1 liter, it would exert a pressure of 22.4 atmospheres (Boyle's law). Morse and Frazer (1905–1913) measured the osmotic pressures of solutions of cane sugar of various concentrations, and found that the pressure per unit concentration was approximately 23.6 atmospheres; that is, 1 mol of sugar (342 g.) in 1 liter of solution exerted an osmotic pressure of 23.6 atmospheres — a number within a few per cent of the pressure exerted by a mol of a gas confined in a space of 1 liter. This shows, therefore, that certain solutions obey (approximately) Avogadro's law.

Solutions of acids, bases, and salts (electrolytes) exhibit abnormally high osmotic pressures, due, we believe, to dissociation. Thus, a solution of potassium chloride has an osmotic pressure 1.88 times as great as that of a corresponding sugar solution (non-electrolyte). Again, we may assume that a molecule of KCl dissociates into two particles. A solution of strontium chloride of the same concentration has an osmotic pressure about 2.7 times as great as has a corresponding sugar solution. In

this case it would appear that 1 molecule dissociates to yield 3 particles:



224. Conclusion. — When the degree of dissociation of acids, bases and salts is calculated from the results arrived at in the study of the freezing points, boiling points, and osmotic pressures of their dilute solutions, it is found that they are in fairly close agreement. Moreover, the chemical behavior of electrolytes indicates quite clearly that dissociation takes place in aqueous solution. We are led to assume, therefore, that in such solutions there is an increase in the number of particles, produced by the dissociation of molecules, such as HCl, KOH, KCl, CuSO₄. We are confirmed in this belief by a study of the electrical conductivity of solutions and of electrolysis.

ELECTROLYSIS

225. Conductors of Electricity. — Conductors of electricity may be divided into two classes:

(1) **Conductors of the First Class, or Metallic Conductors.** The metals and alloys and many sulfides, such as galena and pyrite, are the principal conductors belonging to this class; but a few non-metals, such as graphite (carbon), are conductors. The passage of a current through a conductor of the first class is not accompanied by chemical change. It is believed that an electric current is merely a movement of electrons through a wire or other conductor. Excellent conductors, such as copper and aluminium, appear to have a good many electrons loosely held, while it is probable that non-conductors, such as sulfur and glass, do not have many free electrons.

The number of electrons in motion in a conductor conveying strong currents is enormous. It is possible that each electron does not travel far; it may be passed from atom to atom, each atom losing one electron and then gaining another, the electrons being passed on like a fire bucket from hand to hand.

(2) **Conductors of the Second Class, or Electrolytic Conductors.** Aqueous solutions of acids, bases, and salts (electrolytes) are the principal conductors belonging to this class. *When a current is passed through an electrolyte, chemical change occurs.*

Pure water is practically a non-conductor of electricity. Liquefied hydrogen chloride is also a non-conductor, and it possesses no acid properties; but in aqueous solution it is an excellent

conductor and is an active acid. Dry salts do not conduct electricity under ordinary conditions; but fused salts, such as AgCl and NaCl , and fused alkalis, such as NaOH and KOH , carry the current and are decomposed by it. Aqueous solutions of organic acids, bases, and salts are conductors; but practically all other carbon compounds are non-conductors (non-electrolytes). The general rule is that pure chemical compounds (fused salts and alkalis are exceptions) are not conductors, while acids, bases and salts in aqueous solution (mixtures) are conductors.

It should be known that electrical conductivity is not confined entirely to solutions in water, but is shown by solutions in some other solvents, such as liquid ammonia and acetone.

The electrical conductivity of aqueous solutions of acids, bases, and salts may be demonstrated by immersing platinum electrodes in solutions, say, of HCl , NaOH , and NaCl , contained in separate jars as shown in Fig. 93. A small electric bulb is placed in the circuit. If the solution is a good conductor, the wire glows brightly. Pure water is virtually a non-conductor; also, HCl dissolved in toluene (C_7H_8).

226. Electrolysis. — When a current of electricity is passed through an electrolyte, chemical change occurs. This is known as electrolysis. The plates or conductors through which the current enters and leaves the electrolyte are called the electrodes, — the plate to which the anions are attracted being known as the **anode** (Greek, *the way up*), and the plate to which the cations are attracted, the **cathode** (Greek, *the way down*). The particles which move in the electrolyte, under the guidance of the current, are called **ions** (Greek, meaning *going*). The anions travel or migrate to the anode, and the cations, to the cathode. The terms used in electrolysis were invented by M. Faraday, a British physicist and chemist.

We have seen that when a current of electricity is passed through an electrolyte, substances are set free at the electrodes. Thus, by the electrolysis of hydrochloric acid, equal volumes of hydrogen and of chlorine are liberated (295):

(cathode) $\text{H}_2 \leftarrow 2\text{H} \mid \text{Cl} \rightarrow \text{Cl}_2$ (anode, or positive electrode).

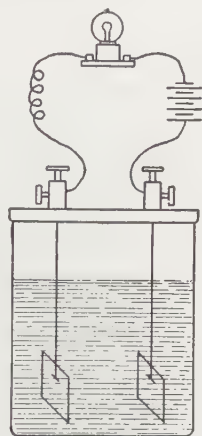


FIG. 93.

Again, when an aqueous solution of a copper salt such as copper sulfate is subjected to electrolysis, copper is deposited on the negative electrode. The passage of an electric current through solutions of various salts is at the basis of electroplating.

In general, experiment shows that hydrogen and the metals appear at the cathode and that chlorine and other electronegative elements, such as oxygen, bromine, and iodine, appear at the anode.

The simplest and most satisfactory way to explain these facts of electrolysis is to assume that molecules of the solute, in the presence of the solvent, dissociate into particles or radicals. As the particles, under the direction of the current, are conveyed or attracted to the opposite electrodes, it is logical to conclude that they are charged with electricity: for example, the dissociation of HCl may be represented thus:



It may be presumed that the hydrogen atom has lost an electron and that the chlorine atom has gained an electron, or is negatively charged. The electrically charged particles are called **ions**, which are atoms or groups of atoms (radicals) carrying charges of electricity.

227. The Arrhenius Theory of Ionization. — As a result of the study of the properties of aqueous solutions, such as the abnormal freezing points, boiling points, and osmotic pressures of electrolytes, as well as their electrical conductivity, Svante Arrhenius (1859–1927), a Swedish chemist, was led to propound his hypothesis of electrolytic dissociation, or ionization, in 1887. This hypothesis has been thoroughly tested by experiment, and has come to be generally known as the theory of ionization. The main assumptions of the theory may be stated thus:

(1) Molecules of acids, bases, and salts, in the presence of water (and certain other solvents), dissociate extensively into electrically charged particles called ions, which serve as the transports for electricity:

		CATIONS		ANIONS
HNO_3	\rightleftharpoons	H^+	+	NO_3^- ,
H_2SO_4	\rightleftharpoons	2H^+	+	$\text{SO}_4^{=}$,
NaOH	\rightleftharpoons	Na^+	+	OH^- ,
Ca(OH)_2	\rightleftharpoons	Ca^{++}	+	2OH^- ,
K_2SO_4	\rightleftharpoons	2K^+	+	$\text{SO}_4^{=}$,
CuCl_2	\rightleftharpoons	Cu^{++}	+	2Cl^- .



SVANTE ARRHENIUS (1859-1927)



MICHAEL FARADAY (1791-1867)

(2) The physical and the chemical properties of electrolytes, as well as their physiological action, are largely dependent upon the nature and concentration of the ions. The ions, therefore, lead an existence which is more or less independent.

Thus, this theory makes it plain why electrolytes differ from non-electrolytes, which do not ionize.

228. The Nature of Ions. — *Ions carry electrical charges. The number of charges corresponds to the valence of the ion, and the positive charges exactly balance the negative.* The cations (hydrogen and the metals) carry positive charges, and the anions (acid radicals) are charged negatively. Since the positive and negative charges are equal, a solution is electrically neutral, as shown by the illustrations in the previous section. This means that equal charges of positive electricity are carried by all univalent cations, and equal charges of negative electricity by univalent anions. Other ions bear charges of electricity proportional to their valences. It is of much interest to note that to each valence of an atom or of a radical there is attached a definite electric charge.

Recent work has shown that ions are more or less hydrated: *e.g.*, the formula for the silver ion might be represented thus: $\text{Ag}(\text{H}_2\text{O})_x^+$.

229. Faraday's Laws. — In 1833–1834 Faraday's investigations in experimental electricity led to the enunciation of his two fundamental laws of electrolysis, which may be stated thus:

First Law: The mass of any substance liberated at an electrode during electrolysis is proportional to the quantity of electricity passed through the electrolytic cell.

Second Law: When the same quantity of electricity passes through different electrolytes, the masses of the substances liberated at the electrodes are proportional to their chemical equivalents.

If a current of 1 ampere (613) be passed through a solution of any silver salt, such as the nitrate, sulfate, or acetate, for one hour, the weight of silver deposited on the cathode is 4.0248 g. The mass of silver is independent, therefore, of the nature of the salt, and it is also independent of conditions, such as temperature, dilution, and current strength. This illustration makes clear the meaning of Faraday's first law of electrolysis.

Faraday's second law of electrolysis may be demonstrated by connecting two or more electrolytic cells in series as shown in Fig. 94. Thus, if a solution of cupric sulfate is introduced into Cell 1, a solution of a silver salt into Cell 2, and dilute sulfuric

acid into Cell 3, and an electric current then passed through the circuit, the quantities of the ions liberated at the electrodes are chemically equivalent.

Experiment shows that 96,500 coulombs of electricity (1 Far-

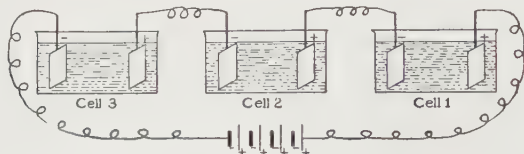


FIG. 94.

day, F) are required to liberate the following masses (weights) which are the chemical equivalents of the elements (29):

Hydrogen.....	1.008 g.
Oxygen.....	8.00 g.
Silver.....	107.88 g.
Chlorine.....	35.46 g.
Copper (Cu^{++}).....	31.785 g.

The weight of an element liberated by passing 96,500 coulombs of electricity through different electrolytes is equal to the gram-atomic weight of the element divided by its valence.

The electrochemical equivalent of an element may be found by dividing its equivalent weight by 96,500; or, expressed mathematically,

$$z = \frac{M}{yF},$$

where z = the weight of ion liberated, M = atomic weight, y = valence, and F = the Faraday (96,500 coulombs). Thus, the *electrochemical equivalent of silver* is

$$\frac{107.88}{96,500} = 0.001118 \text{ g. per coulomb.}$$

This is the mass of silver deposited from a solution of a silver salt by a current of 1 ampere in one second. A current of 1 ampere liberates or deposits 1 electrochemical equivalent of an ion or element in one second.

The **coulomb** is the unit quantity of electricity. In one second 1 coulomb of electricity is transported past a given point by a

current of 1 ampere. The **ampere** is represented by the current which will deposit silver from a solution of silver nitrate at the rate of 0.001118 g. per second (see Chap. XXXIV).

230. **The Source and Nature of the Electric Charges.** — The facts pertaining to electrolysis and electrical conductivity of electrolytes led to the theory that ionization is brought about through the agency of the solvent, as represented, for example, by the following equilibrium equation:



When an electrolysis is carried out, the current is directive, *i.e.*, the ions transport their own charges of electricity to the electrodes, under the pilotage of the current.

According to the modern view, matter is electrical in nature (92). An atom of an element is assumed to have a nucleus which consists of a definite number of positively charged units, and for each positive unit in excess of the nuclear electrons there is a negative unit (electron) located outside the nucleus. Since the positive and negative units are equal, the atom as a whole is neutral. The electron (negative particle of electricity) appears to have a mass about 1/1845 of that of an atom of hydrogen.

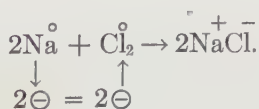
Some atoms have a tendency to lose one or more electrons, while others have a tendency to take them on. When an atom loses an electron, it assumes a positive charge; but when an atom takes on an electron, it is negatively charged. Representing an electron by the symbol \ominus , we have in the case of sodium the following:



When an atom of chlorine takes on an electron, it assumes a negative charge:



Now, when sodium and chlorine interact to form NaCl, much energy is liberated. It is reasonable to assume that this display of energy is brought about by the passage of electrons from sodium atoms to chlorine atoms to form molecules of sodium chloride:



We may assume that the particles of opposite charges constituting the molecule NaCl are held together, in part at least, by electrical attraction; that is, sodium chloride is a polarized compound (88), being at least potentially ionized. In the absence of water (or other ionizing media) the oppositely charged particles are closely bound together; but when the salt is dissolved in water, the molecules ionize, *i.e.*, the charged particles are forced apart by the solvent. How does the solvent accomplish this?

The following illustration may aid in answering the question. If two insulated balls bearing opposite charges of electricity were suspended comparatively near each other, the attraction between the bodies would be directly proportional to the product of the charges and inversely proportional to the square of the distance between them.¹ The force of the attraction would also depend upon the medium surrounding the balls. If glass were substituted for air, the force of attraction would be reduced to about 1/3; and if water were the medium, the force of attraction would be about 1/80 as compared with air. In other words, *the force of attraction between the charged balls is inversely proportional to the dielectric constant of the medium.* Therefore it is easy to see that when NaCl is dissolved in water (a solvent with a very high dielectric constant), the tendency for the molecules to ionize is great.

Certain solvents, such as benzene, toluene, and ether, have little or no ionizing effect. Thus, when HCl (dry) is dissolved in toluene the solution does not conduct electricity, nor has it any of the properties of an acid. Liquid sulfur dioxide and ammonia show the same effects as does water, but to a different degree.

The *dielectric constants* of a few common liquids are as follows:

Water.....	81
Methyl alcohol.....	32
Ethyl alcohol.....	22
Acetone.....	22
Ammonia.....	22
Sulfur dioxide.....	15
Chloroform.....	5
Ether.....	4
Benzene and Toluene.....	2

¹ $F = \frac{Q \times Q^1}{kd^2}$, where F is the attractive force, Q and Q^1 , the charges, d , the distance between the charged bodies, and k , the dielectric constant of the medium.

231. Nomenclature of Ions. — The system illustrated by the following table may be employed in naming ionic substances:

Name of Compound	Formula	Name and Formula of Cation	Name and Formula of Anion
Sodium chloride.....	NaCl	Sodium-ion, Na ⁺	Chloride-ion, Cl ⁻
Silver nitrate.....	AgNO ₃	Silver-ion, Ag ⁺	Nitrate-ion, NO ₃ ⁻
Cupric sulfate.....	CuSO ₄	Cupric-ion, Cu ⁺⁺	Sulfate-ion, SO ₄ ⁼
Ferrous bromide.....	FeBr ₂	Ferrous-ion, Fe ⁺⁺	Bromide-ion, Br ⁻
Potassium bisulfate....	KHSO ₄	Potassium-ion, K ⁺	Bisulfate-ion, HSO ₄ ⁻
Ammonium carbonate..	(NH ₄) ₂ CO ₃	Ammonium-ion, NH ₄ ⁺	Carbonate-ion, CO ₃ ⁼
Calcium hydroxide.....	Ca(OH) ₂	Calcium-ion, Ca ⁺⁺	Hydroxide-ion, OH ⁻
Chloric acid.....	HClO ₃	Hydrogen-ion, H ⁺	Chlorate-ion, ClO ₃ ⁻

232. The Degree of Ionization. — According to the Arrhenius theory of ionization, the fraction of the solute ionized increases with dilution, and becomes complete, or practically so, in very dilute solutions. This is what the kinetic theory would lead one to expect. As the dilution increases, the ions are separated farther and farther and have fewer opportunities of recombining to form molecules. In any particular dilution an equilibrium is established, which may be displaced forward by adding more solvent, and backward by evaporating solvent:



As previously stated (64), the examination of crystals of sodium chloride by X-rays indicates that this salt consists not of molecules of NaCl, but of ions (Na⁺ and Cl⁻) arranged in a space lattice; in solution such a substance would simply break up or fall apart into its ions. In its modern form, therefore, the ionic theory assumes that even solid salts are composed of ions, and it is now common to assume complete ionization of salts, both in the solid state and in solution.

EXERCISES

1. Give several lines of evidence that acids, bases, and salts dissociate in aqueous solution.
2. Define and illustrate the following terms: (1) electrolyte; (2) electrolysis; (3) ion; (4) cation; (5) anion; (6) ionization.
3. Outline the Arrhenius theory of ionization. When did he first propose the theory? State, if you can, some objections to the theory.
4. What classes of substances and solutions are conductors of electricity? What part is the electron supposed to play in the conductance of a metal?

5. State and explain the laws of Faraday.

6. Fully illustrate the following statement: "To each valency of an atom or radical there is attached a definite electric charge."

7. Define the following terms: coulomb; Faraday; electrochemical equivalent; ampere; and volt.

8. How many seconds would be required for a current of 1 ampere to deposit 2.1576 g. of silver from a solution of silver nitrate?

9. A quantity of electricity which liberated 30.5 cc. of hydrogen, measured over water at 20° C. and 765 mm., was also used in the electrolysis of cupric sulfate. Calculate the weight of copper deposited.

10. How many coulombs of electricity would be required to deposit, or liberate, a gram-atomic weight of each of the following elements: hydrogen, oxygen, chlorine, zinc, silver, iron (Fe^{++}), cadmium, and copper (Cu^{++})? Explain.

11. How much time would be required to deposit 0.1079 g. of silver by passing a current of 1 coulomb per second through a 1-ampere lamp? through 2 half-ampere lamps in parallel?

12. Discuss the nature of ions. Show by equilibrium equations how the following compounds ionize, giving the names of the ions: H_2SO_4 , FeCl_2 , HgNO_3 , $\text{Hg}(\text{NO}_3)_2$, $\text{Ba}(\text{OH})_2$, NaHCO_3 , KNO_2 , NaClO , $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$, and $(\text{NH}_4)_2\text{C}_2\text{O}_4$.

13. How is electricity conducted through electrolytes? What is the function of the solvent? of the current supplied by the battery?

14. What is known about the ionization of such salts as NaCl and KCl , both in the solid state and in aqueous solution? What is supposed to be the source of the ionic charges?

15. According to Arrhenius, how does the quantity of solvent affect the degree of ionization?

16. What do you understand by the term "dielectric"? What is the dielectric constant of water? What is the relation of the dielectric to the ionizing power of a solvent?

READINGS AND REFERENCES

ARRHENIUS. *Chemistry in Modern Life*, Chap. X.

FOSTER. *The Romance of Chemistry*, Chap. X.

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LOWRY. *Inorganic Chemistry*, Chap. XVIII.

MOORE. *History of Chemistry*, pp. 234-251.

TAYLOR. *Elementary Physical Chemistry*, pp. 373-388.

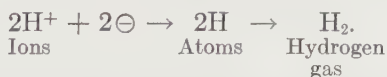
CHAPTER XIII

SOME APPLICATIONS OF THE IONIC THEORY

233. **Application of the Ionic Theory to the Explanation of Electrolysis.** — Electrolysis can be explained most satisfactorily in terms of the ionic theory. Let us apply the theory to the electrolysis of hydrochloric acid. When hydrogen chloride is dissolved in water, it ionizes thus:



When an electric current is passed through hydrochloric acid, the hydrogen ions are attracted by the cathode and repelled by the anode, while the chlorine ions are attracted by the anode and repelled by the cathode. In other words, the ions with opposite charges migrate to the electrodes, under the pilotage of the electricity furnished by the battery. At the electrodes electrochemical changes occur, *i.e.*, the ions are discharged. At the cathode the discharge of the hydrogen-ion may be represented thus:



This means that 2 electrons, supplied by the negatively charged electrode, unite with 2 hydrogen ions to form atoms, which in turn form free molecular hydrogen (H_2).

Note that the hydrogen-ion and free hydrogen are different substances. The former has a sour taste and turns blue litmus red, while the latter is a tasteless gas. Their energy content is different.

At the anode the change may be represented thus:



Atoms of chlorine unite to form free molecular chlorine (Cl_2), which escapes at the anode. The discharge of an anion means the loss of one or more electrons, which escape by way of the anode, and then pass through the wire to the battery.

During electrolysis there is a circulation of electrons from the negative pole of the battery through the electrolyte to the positive pole. It is the function of the battery (or other source of electricity) to furnish electrons (see Fig. 95).

The chemical changes connected with the electrolysis of hydrochloric acid are *primary*, for the ions are discharged at the electrodes and do not interact with the solvent.

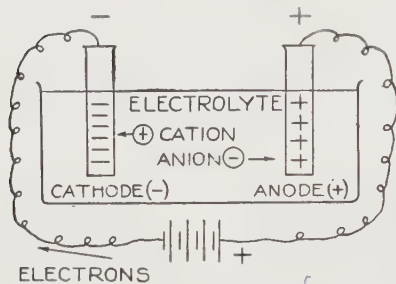
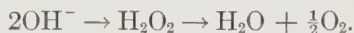


FIG. 95.

The electrolysis of other electrolytes is analogous to that of hydrochloric acid, but in the case of certain substances *secondary products* are obtained. The electrolysis of sulfuric acid is a good illustrative example.

According to one theory, the hydroxide ions produced by the slight ionization of water discharge instead of sulfate ions, and then react with each other ultimately to form water and oxygen:



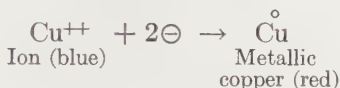
Again, when nitrates are electrolyzed, secondary products are obtained. To illustrate, the electrolysis of a solution of KNO_3 may be carried out in a V-shaped tube (Fig. 99). The solution is colored by the addition of a solution of neutral litmus before the current is turned on. In the course of a few minutes, the litmus turns blue around the cathode and hydrogen is liberated at that electrode, while the solution turns red around the anode and oxygen is liberated there, as in case of sulfuric acid. K^+ migrates to the cathode, but it is not discharged. Instead, hydrogen is liberated. This is explained by assuming that molecules of water dissociate very slightly, and that the hydrogen ions are discharged in place of potassium ions:



Ions of the active elements are more difficult to discharge than are the less active ones. When the hydrogen ions are discharged, hydrogen escapes at the cathode, and hydroxide ions (OH^-) are left in the solution along with potassium ions (K^+). In

other words, potassium hydroxide, which is highly dissociated, is formed around the cathode.

Electroplating is based upon the discharge of cations from salts of metals. Thus, in case of copper, the change may be represented as follows:



Note that cupric-ion (Cu^{++}) and metallic copper (Cu) are different substances. The former is blue and soluble in water, while the latter is red, insoluble in water, and has more energy associated with it than has cupric-ion. Also note that Na^+ and Na stand for different substances.

234. Migration of the Ions. — That the ions migrate or travel toward the electrodes during electrolysis, may be demonstrated by the following *experiment*:

A portion of cupric sulfate is dissolved in warm water containing about 5 per cent of agar-agar, and the lower part of a large U-tube (Fig. 96) is filled with this mixture. When the mixture cools, it forms a jelly, thus keeping the cupric sulfate in place when other liquids are poured into the tube. A thin layer of grains of charcoal is placed upon the surface of the jelly to serve as a boundary line. A solution of potassium nitrate (a colorless conductor) is now poured into each limb of the tube, some agar-agar being added to the lower portion of the liquid in order to stiffen it. Finally, platinum electrodes are introduced into the upper portion of the liquid, and the tube is immersed in water in which there is plenty of ice to prevent the melting of the jelly when the current is passed through. A current (*e.g.*, 110 volts, and a 50-watt lamp in series with the cell) is turned on, and in the course of a few minutes a drift of the blue cupric ions toward the cathode and away from the anode may be observed. This movement of the ions under the pilotage of the current is called "ionic migration." The sulfate ions migrate toward the anode, but they are colorless and hence invisible. It may be shown, however, that they are present by placing a few drops of a solution of a barium

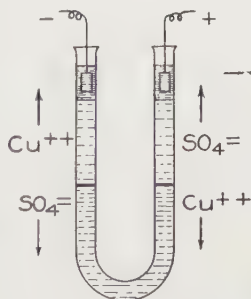
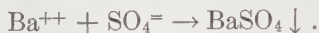


FIG. 96.

salt in the jelly a short distance above the charcoal on the positive side of the tube. Barium sulfate (white) is formed:



The **speed of ions**, under given conditions, has been carefully determined by experiment and is different for different ions. The hydrogen-ion has the greatest speed, and the hydroxide-ion (OH^-) is second. *Moving ions are influenced by two forces, namely, (1) the driving force of the potential gradient, and (2) the frictional resistance of the solvent.* The latter is very great. According to Kohlrausch, it is necessary to apply no less than a total force of 1,500,000 tons in order to pull 1 gram-molecule of potassium ions (K^+) through a solution with a speed of 1 cm. per second.

With electrodes 1 cm. apart, and with a difference of electrical potential of 1 volt between the electrodes of the vessel, the *speeds in centimeters per hour* of a few ions are:

H^+	10.8	Na^+	1.26	Ag^+	1.66
OH^-	5.6	Cl^-	2.12	NO_3^-	1.91

235. Electrical Conductivity and Ionization. — Measurement of the electrical conductivity (or conductance) of electrolytes, according to Arrhenius, furnishes valuable data for calculating the fraction of the molecules ionized. When these results are compared with those obtained by independent methods, such as the lowering of the freezing point, it is found that the agreement is ordinarily as close as one could expect. This may be illustrated by the table given below, which compares the degree of ionization by the conductivity and freezing point methods. The conductivity measurements were made by independent experimenters.

The following *experiment* serves to illustrate the relation of electrical conductivity to ionic concentration:

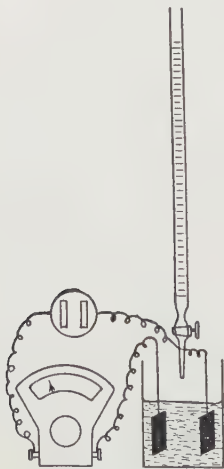
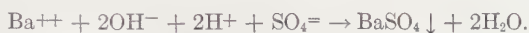


FIG. 97.

A solution of $N/10$ barium hydroxide (approximately) is connected in series with a battery and ammeter (Fig. 97). The battery should be so weak that the ammeter registers between 22–25 milliamperes when thus connected. $2N$ sulfuric acid is now allowed to run into the barium hydroxide

solution, drop by drop, with constant stirring. The reaction which occurs may be represented thus:



When just enough sulfuric acid has been added to remove all the Ba^{++} , the conductivity of the solution is reduced practically to zero (why?). By adding an excess of sulfuric acid, the conductivity of the solution gradually increases, as may be seen by following the needle of the ammeter.

DEGREE OF IONIZATION AS SHOWN BY THE CONDUCTIVITY
AND FREEZING POINT METHODS

Formula of Compound	Molar Concentration (M)	Percentage of Ionization Calculated from Conductivity	Percentage of Ionization Calculated from Freezing Point
NaOH	0.02	91.6	86.0
	0.05	89.8	86.0
	0.10	88.1	83.0
	0.20	85.7	83.0
	0.01	93.2	93.0
$(\text{NH}_4)\text{NO}_3$	0.02	91.4	90.0
	0.05	87.2	87.0
	0.10	84.5	84.0
	0.20	80.5	79.0

The fraction of an acid, base, or salt ionized depends, according to the theory of Arrhenius, primarily upon the dilution of the solution and upon the nature of the substance.

Apparent Fraction Ionized in 0.1 N Solutions at 18°.

ACIDS

Hydrochloric acid (H^+ , Cl^-)	0.92
Nitric acid (H^+ , NO_3^-)	0.92
Sulfuric acid (2H^+ , $\text{SO}_4^{=}$)	0.61
Acetic acid (H^+ , $\text{C}_2\text{H}_3\text{O}_2^-$)	0.0134
Carbonic acid (H^+ , HCO_3^-)	0.0017
Hydrogen sulfide (H^+ , HS^-)	0.0007
Boric acid (H^+ , H_2BO_3^-)	0.0001
Hydrocyanic acid (H^+ , CN^-)	0.0001

BASES

Sodium hydroxide (Na^+ , OH^-)	0.91
Potassium hydroxide (K^+ , OH^-)	0.91
Barium hydroxide (Ba^{++} , 2OH^-)	0.81
Ammonium hydroxide (NH_4^+ , OH^-)	0.013

SALTS

Potassium chloride (K^+ , Cl^-)	0.86
Sodium chloride (Na^+ , Cl^-)	0.85
Ammonium nitrate (NH_4^+ , NO_3^-)	0.85
Potassium chlorate (K^+ , ClO_3^-)	0.83
Sodium bicarbonate (Na^+ , HCO_3^-)	0.78
Magnesium chloride (Mg^{++} , $2Cl^-$)	0.73
Magnesium sulfate (Mg^{++} , $SO_4^{=}$)	0.42
Zinc sulfate (Zn^{++} , $SO_4^{=}$)	0.41
Mercuric chloride (Hg^{++} , $2Cl^-$)	0.01
Mercuric cyanide (Hg^{++} , $2CN^-$)	trace

Water is only slightly ionized, the fraction ionized being about 0.0000001 at 25° C.:



Water is therefore practically a non-conductor of electricity, and is a neutral substance. The ionization of water is so slight that we need about 10,000,000 liters of the substance to supply 1 gram-atom of hydrogen-ion. Stated another way, about 60,000 barrels of water are required to furnish 1 g. of the hydrogen-ion.

It is now quite common to express extremely faint acidities and alkalinities in what is known as **pH-values**, or **hydrogen-ion indexes**. By the pH-value we mean the logarithm of the number of liters of a solution which must be taken in order to contain 1 gram-ion of hydrogen. Since 10,000,000 liters of water are required to furnish a gram-ion of hydrogen, the pH-value of water is 7, the logarithm of 10,000,000. The pH-value of other neutral solutions is also 7. Acid solutions have a pH-value less than 7, while that of alkaline solutions is greater. The pH-value of normal human blood is 7.5, thus indicating that it is slightly alkaline. Certain experiments have indicated that the maximum hydrogen-ion concentration of the contents of the human stomach is slightly different in different individuals, varying between $pH = 1$ and $pH = 2.5$.

The following table shows the *change in fraction ionized with change in concentration*.

Concentrated (95 per cent) sulfuric acid is a very poor conductor of electricity, for the fraction ionized is only 0.01. The fraction ionized in conc. (62 per cent) nitric acid is 0.09, and in conc. (35 per cent) hydrochloric acid is 0.13.

An examination of these tables shows that the ionization of electrolytes varies, according to the conductivity method, within

wide limits, even in the case of certain solutions of identical concentration. Thus, the percentage of molecules ionized in 0.1 *N* solutions of hydrochloric acid is 92, while acetic acid of the same concentration is only 1.34 per cent dissociated, and carbonic acid 0.17 per cent.

Concentration (Normal)	(NH ₄)NO ₃	MgCl ₂	MgSO ₄
0.0006	0.993	0.950	0.874
0.001	0.987	0.941	0.850
0.002	0.975	0.926	0.798
0.006	0.948	0.889	0.699
0.01	0.932	0.870	0.648
0.03	0.896	0.804	0.530
0.05	0.872	0.771	0.482
0.10	0.845	0.728	0.420
0.50	0.749	0.614	0.299
1.00	0.704	0.545	0.245

Likewise, bases and salts show varying degrees of dissociation. The solutions containing highly ionized substances are the best conductors of electricity. *In general, according to the theory of Arrhenius, the chemical activity of an electrolyte depends upon the fraction of the molecules ionized.* Thus, hydrochloric acid is called a "strong" (active) acid, for hydrogen chloride is highly dissociated in dilute and moderately dilute solutions; that is, there is a high concentration of hydrogen-ion (H^+), upon which the activity of an acid depends. Acetic acid is a "weak" acid, and carbonic acid is very feeble.

236. Chemical Activity and Ionization. — Acids, bases, and salts may be divided into the following classes:

(I) Acids.

(1) *Strong or Active Acids:* e.g., hydrochloric and nitric acids. These acids, when diluted, furnish a relatively high concentration of the hydrogen-ion (H^+), and are very active chemically.

(2) *Moderately Active Acids:* e.g., phosphoric and hydrofluoric acids. These acids are less highly ionized than are those of class (1), and are, therefore, only fairly active.

(3) *Weak Acids:* e.g., acetic, carbonic, and boric acids. Even very dilute solutions of this class of acids are only slightly ionized; therefore they are very poor conductors of the electric current and show but little chemical activity as compared with strong acids.

(II) Bases.

(1) *Strong Bases:* e.g., the hydroxides of the alkali and of the alkaline earth metals, such as NaOH, KOH, and Ca(OH)₂. Dilute solutions of these bases furnish a relatively high concentration of the hydroxide-ion (OH⁻), and are exceedingly active as bases.

(2) *Moderately Active Bases:* e.g., silver hydroxide.

(3) *Weak Bases:* e.g., ammonium hydroxide, NH₄OH.

(III) **Salts.** Salts, as a rule, are highly ionized in dilute aqueous solutions. The salts of mercury are exceptions, being but feebly ionized. Cadmium halides are not highly ionized.

Salts yielding univalent ions are more highly ionized than are those yielding ions having more charges (Compare KCl and MgSO₄).

237. Ionic Equilibrium. — When molecules of acids, bases, or salts dissociate in the presence of an ionizing medium, the action is reversible:



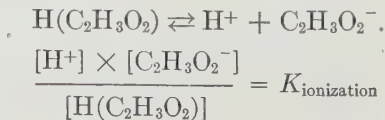
The percentage of dissociation in a 0.1 *N* solution of magnesium sulfate is about 42, while it is only 24.5 in a normal solution. The equilibrium point may be displaced to the right by adding water, and to the left by removing the solvent. If all the solvent be removed, the solid salt will remain, i.e., all the ions unite to form molecules. The dissociation, according to the Arrhenius theory, is practically complete in very dilute solutions: e.g., (NH₄)NO₃ is 99.3 per cent dissociated when the normal concentration of the solution is 0.0006.

The formulation at equilibrium, taking acetic acid as an illustration, may be expressed thus:

$$\frac{[\text{H}^+] \times [\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = K, \text{ where } [\text{H}^+] \text{ and } [\text{C}_2\text{H}_3\text{O}_2^-]$$

represent the concentrations of the ions, [HC₂H₃O₂] the concentration of the molecules, and *K* the **Ionization Constant**.

Example. — A 0.1 normal (= 0.1 molar) solution of acetic acid is 1.34 per cent ionized (235). What is the ionization constant *K*?



As the fraction ionized is 0.0134, the concentration of each of the ions is $0.1 \times 0.0134 = 0.00134$, and the concentration of the non-ionized acid is $0.1 - 0.00134 = 0.09866$; therefore,

$$K = \frac{(0.1 \times 0.0134)^2}{(0.09866)} = 0.0000182.$$

Ionic equilibria may be displaced as follows:

(1) **By changing the amount of solvent.**

When the solution is very dilute, the compound is highly ionized and the ions are relatively far apart; but when the solvent is removed, the ions encounter each other more frequently and unite to form molecules. The displacement of the equilibrium point may be shown by the following *experiment*:

Water is added little by little to about 1 g. of cupric bromide, CuBr_2 , contained in a large test-tube, until the solution changes from deep brown to green, and then to blue. The brown color is due to molecules of cupric bromide, and the blue color to cupricion (Cu^{++}). The green is caused by a mixture of CuBr_2 and Cu^{++} :

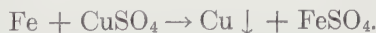


By evaporation of the solvent, cupric bromide may be recovered.

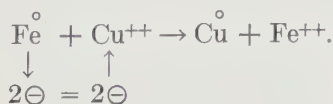
(2) **By changing the concentration of one of the ions.**

By adding finely divided KBr to a greenish or bluish solution of CuBr_2 , the equilibrium is displaced; for the ions (Cu^{++} and Br^-) interact to form molecules (CuBr_2). This is shown by the change in the color of the solution from blue or green to brown.

238. Displacement of Ions. — When solutions of certain compounds are treated with elementary substances, a familiar change known as displacement occurs. Thus, when a bright iron spatula is suspended for a few minutes in a solution of copper sulfate the spatula becomes coated with copper (red):



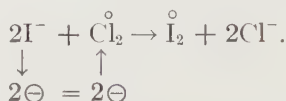
In terms of ions and electrons, the chemical change may be represented thus:



Since iron is more active than copper, its atom may be regarded as giving two electrons to the copper-ion, which is thus transformed into metallic copper.

In a similar manner, zinc displaces lead. This may be shown by suspending a rod of zinc in a solution of lead nitrate. On standing, lead separates and the larger portion attaches itself to the remaining zinc. Copper and mercury also displace silver. This may be shown very strikingly by suspending a bag containing mercury, in a solution of silver nitrate. Silver separates and forms numerous spangles radiating from the bag containing mercury (12).

Likewise, anions may be displaced. Thus, chlorine displaces iodine from solutions containing iodides:

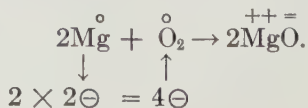


In this case chlorine is a more active electronegative element than is iodine, so the iodide ions supply electrons to change free chlorine to chloride ions.

The order of activity of the metals (126) gives a series which is often called the **electromotive series** of the metals; for when the electrolysis of normal solutions of their salts is carried out, the electromotive force of the current required to liberate, or deposit, each metal is less than that for any metal preceding it in the series. This means that it requires less difference of potential to deposit such metals as silver and gold than it does to deposit cadmium and nickel.

We see, then, that *the more active metals have a greater tendency to lose electrons, and thus pass from the elementary state into the ionic condition.* The ionic theory furnishes a very satisfactory explanation of the displacement of ions, as it does of electrolysis and of conductivity.

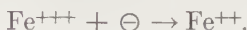
239. Oxidation and Reduction and Electrons. — *Oxidation consists in the loss of electrons by atoms or ions, and reduction is the converse, i.e., the addition of electrons.* Thus, when magnesium is burned, the change may be represented as follows:



Again, by treating a solution of ferric chloride with hydrogen sulfide, the former is reduced to ferrous chloride. The skeleton equation is —



In FeCl_3 , iron has a positive valence of 3 (Fe^{+++}). In the case under consideration Fe^{+++} is the oxidizing agent, and when it is reduced to the bivalent ion (Fe^{++}), there is a gain of one electron:



In H_2S , sulfur has a negative valence of 2 ($\text{S}^{=}$). The sulfide-ion is a reducing agent, and is capable of supplying 2 electrons to reduce 2Fe^{+++} :



The equation may now be balanced:



Free sulfur is obtained, which has no active valence, and Fe^{+++} is reduced (gains an electron) and $\text{S}^{=}$ is oxidized, or loses electrons.

Fundamentally, then, **oxidation may be regarded as the loss of electrons by atoms or ions, while reduction is the converse**, as summarized below:

Oxidation



Reduction

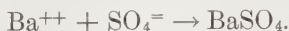
The oxidation-reduction reaction will be treated much more fully in Chap. XV.

We see, therefore, that equations may be balanced by the ion-electron method.

240. The Ionic Theory and Chemical Analysis. — The ionic theory simplifies the analysis of solutions of acids, bases, and salts; for the detection of these substances is reduced to the identification of their ions. Thus, silver is common to all silver salts. The silver-ion may be detected by adding a solution of a chloride to a solution of a silver salt:



Likewise, barium-ion is a test for sulfate-ion, which is present in sulfuric acid and in solutions of its salts:



The colors of certain ions are helpful in their identification: *e.g.*, Cu^{++} is blue; Cr_2O_7^- , orange-red; and MnO_4^- , purple.

Again, hydrogen-ion is common to all acids, just as hydroxide-ion is common to bases.

As expressed by Ostwald, *salts are characterized by the fact that in solution their components (ions) give individual reactions which are in each case independent of the other component present in the salt.*

EXERCISES

1. Apply the ionic theory to the explanation of the electrolysis of solutions of the following compounds: CdSO_4 , Na_2SO_4 , $\text{Cu}(\text{NO}_3)_2$, and $\text{Ba}(\text{OH})_2$.
2. Apply the ionic theory to the following:
 - (1) The electrolysis of a solution of CuSO_4 between copper electrodes.
 - (2) The electrolysis of a solution of AgNO_3 between silver electrodes.
 - (3) The electrolysis of fused AgCl .
3. Show that electrolysis may be explained satisfactorily by assuming the existence of only one kind of electrical charge (the electron).
4. What is the connection between the electrical conductivity of solutions and the degree of ionization?
5. What important conclusion may be drawn from the fact that the percentage of dissociation of $(\text{NH}_4)\text{NO}_3$, calculated from the conductivity of its solutions, agrees closely with that calculated from the depression of the freezing point?
6. Upon what does the chemical activity of an electrolyte depend? Illustrate. Classify common acids and bases as to their activity or strength.
7. Explain why concentrated acids are such poor conductors of electricity.
8. Does water ionize? Explain and also illustrate what is meant by the *pH*-value of solutions.
9. Cite experimental evidence to show that ions actually migrate in solutions through which an electric current is being passed. How do you explain the fact that the speed of ions is so slow?
10. Why will normal hydrochloric acid cause a more rapid evolution of hydrogen when zinc is added than will normal acetic acid?
11. Formulate the ionic equilibrium when NH_4OH is dissolved in water; also for PbCl_2 .
12. How may ionic equilibria be displaced? Fully illustrate.
13. What is meant by the displacement of ions? Illustrate by means of a number of examples. Explain the meaning of the electromotive series of the metals.
14. Write several equations to illustrate the oxidation-reduction reaction and explain them in terms of ions and electrons.
15. How many different salts of the ordinary type, such as K_2SO_4 and Na_2CO_3 , could be formed by the union of 10 different cations with 10 different

anions? In the identification of these salts by chemical tests, how many different kinds of tests would be necessary?

(16) If 0.01 *M* acetic acid is 4.17 per cent ionized, find the ionization constant *K*. Compare this with the value previously found (237).

(17) Barium hydroxide solution and dilute sulfuric acid are both excellent conductors of electricity, but when a given amount of the former is treated with an equivalent of the latter, the conductivity is reduced to zero. Explain what would be the effect of adding an excess of the acid; of the base.

READINGS AND REFERENCES

Chemistry in Industry, Vol. II, Chap. VIII.

PARTINGTON. Textbook of Inorganic Chemistry, Chap. XVI.

SMITH-KENDALL. Inorganic Chemistry, Chap. XVIII.

CHAPTER XIV

ACIDS, BASES, AND SALTS. IONIC EQUILIBRIA

241. **Acids.** — An acid ionizes to produce the hydrogen-ion (H^+), as well as an anion. Acids of the same concentration vary greatly in activity, which depends upon the concentration of hydrogen-ion. To illustrate, 0.1 *N* hydrochloric acid is about 70 times as active as acetic acid of the same concentration, for the former is 92 per cent ionized and the latter 1.3. If, therefore, pieces of zinc of equal size are treated with equivalent solutions of these acids, the speed of the action with hydrochloric acid is greater than that in case of acetic acid; but the amount of hydrogen ultimately set free is the same in both cases.

The strength or activity of acids may be compared by adding a mixture of two acids to a solution of the same base, the base not being present in sufficient quantity to neutralize both acids. (Predict the result when two acids of different strength compete for the same base.)

Indicators also may be employed to secure information concerning the strength of acids. Thus, syrup of violets turns green in the presence of acetic acid, but is not affected by carbonic acid. The latter acid is, however, strong enough to redden blue litmus.

Hydrogen-ion is colorless, univalent, possesses a sour taste, reddens litmus, is soluble in water, and is displaced by the metals above it in the electromotive series (126). This explains clearly why metals are treated with diluted acids in the preparation of hydrogen, and why the metals below hydrogen do not yield the latter when treated with acids.

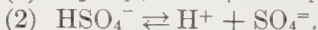
242. **Classes of Acids.** — Acids may be divided into classes based upon the number of ionizable hydrogen atoms contained in a molecule of the acid. The following are some of the most important:

(I) **Monobasic Acids:** *e.g.*, HCl , HNO_3 , and $H(C_2H_3O_2)$. A molecule of a monobasic acid ionizes thus:



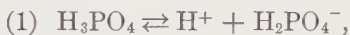
(II) **Dibasic Acids:** *e.g.*, H_2SO_4 , H_2CO_3 , H_2S , $H_2C_2O_4$ (oxalic acid), and $H_2(C_4H_4O_6)$ (tartaric acid). A molecule of a dibasic

acid contains two ionizable hydrogen atoms:



The bisulfate-ion is present in considerable concentration in fairly concentrated sulfuric acid, but in dilute solutions is largely ionized to yield a second hydrogen-ion.

(III) **Tribasic Acids:** *e.g.*, H_3PO_4 and H_3AsO_4 (arsenic acid). A molecule of a tribasic acid contains three atoms of ionizable hydrogen:



A high degree of dilution favors the formation of the phosphate-ion, $\text{PO}_4^{=}$.

243. **Bases.** — A base ionizes to produce hydroxide-ion (OH^-), as well as a cation:



Bases of the same concentration vary in strength or activity. Thus, 0.1 *N* NaOH is about 70 times as active as a solution of $(\text{NH}_4)\text{OH}$ of the same concentration, for the activity of a base depends upon the concentration of the hydroxide-ion.

The **hydroxide-ion** is colorless, univalent, possesses a soapy taste and feeling, turns litmus blue, and readily combines with hydrogen-ion to form water:

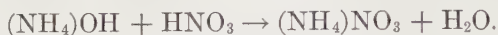


Sodium hydroxide is a typical base. Its solution is an excellent conductor of the electric current and is chemically active.

Hydroxides of metals do not volatilize, as a rule, when heated. The name base (foundation) is due to the fact that this class of substances is generally the non-volatile constituent of a salt; while the acid constituent usually is volatile, when heated. Ammonium hydroxide is unstable and volatile.

244. **Classes of Bases.** — Bases may be divided into classes which are determined by the number of hydroxyl groups in a molecule of the base. They are called *monacid*, *diacid*, or *triacid* bases, etc., depending upon the number of molecules of a monobasic acid required to neutralize one molecule of the base:

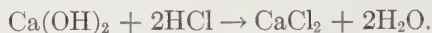
(I) **Monacid Bases:** *e.g.*, NaOH, KOH, and (NH₄)OH. The interaction of one of these bases with a monobasic acid may be illustrated thus:



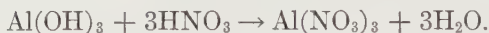
(II) **Diacid Bases:** *e.g.*, Ca(OH)₂, Sr(OH)₂, Ba(OH)₂, and Mg(OH)₂. A molecule of one of these bases ionizes thus:



Two molecules of a monobasic acid are required to neutralize one molecule of the base:



(III) **Triacid Bases:** *e.g.*, Al(OH)₃ and Fe(OH)₃. Three molecules of a monobasic acid are required to interact with one of the base:



245. Salts. — Salts may be regarded as derivatives of acids, being formed by substituting metallic radicals for all or part of the hydrogen in the molecules of acids. Aqueous solutions of salts contain a cation and an anion:



Solutions of different salts vary greatly in properties.

Common salt is typical of this class of compounds. This salt has been prepared and used since very early times. An aqueous solution of sodium chloride is a good conductor of electricity and has a characteristic taste or savor. Robert Boyle, in 1680, defined a "salt" as a substance "easily soluble in water" and "possessing a savour, whether good or evil." Salts differ so much in their properties, however, that Boyle's definition does not cover all cases.

Many salts occur in nature in great abundance. Rock-salt sometimes occurs in beds several thousand feet thick. It is the most abundant soluble salt. The most valuable known soluble salt-deposits are at Stassfurt, in the province of Magdeburg, Germany. The Stassfurt salt-beds contain immense quantities of compounds of potassium, sodium, magnesium, and calcium, which occur largely as chlorides and sulfates. Salt springs were known in this region as early as the thirteenth century, but borings

were not made until about the middle of the nineteenth century, rock-salt having been mined. The material excavated with the rock-salt was thrown away, for it was thought to be worthless. Rose and Rammelsberg investigated this refuse thoroughly, and discovered that it was rich in potassium and magnesium salts, which led to the great potash industry of Germany. One of the most valuable salts obtained is potassium chloride, the first works for its extraction having been erected in 1861. It is estimated that the Stassfurt deposits yield about 5,000,000 tons of crude potassium salts annually.

The Stassfurt salt-beds are about 3,000 feet deep, and were no doubt formed as the result of the evaporation of sea-water extending over a period of many thousand years. The volume of sea-water evaporated represents a total depth of 30 miles. Vast quantities of salts, including certain compounds of potassium, are in the water of the Dead Sea, and it is likely that these salts will be recovered, or that valuable chemicals will be produced from them.

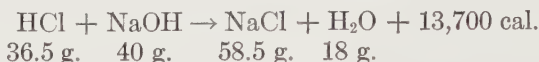
One of the most useful salts found in nature is sodium nitrate, or Chile saltpeter. This salt occurs in beds extending about 250 miles along the West Coast of South America. The average width of the beds is over 2 miles, while the average depth is about 5 feet. The salt occurs in a rainless zone, and is locally known as *caliche*. The better grades of the crude material contain from about 50 to 75 per cent of sodium nitrate and from 20 to 40 per cent of sodium chloride. Other salts also are present, as well as some organic matter: *e.g.*, guano. Caliche is treated with hot water, and the insoluble matter allowed to settle. The liquid is then run into cisterns, where much of the sodium chloride crystallizes out. From the mother-liquor sodium nitrate is obtained by crystallization.

Over 55,000,000 tons of Chile saltpeter have been mined since its discovery early in the last century. It is of very great economic importance, for it is not only a source of nitric acid, but is an excellent fertilizer. In 1825 the first ship-load of Chile saltpeter was taken to Europe, but was dumped into the sea, for nobody would buy it. In 1914 the United States was importing about 500,000 tons annually, and Germany about 700,000 tons.

There are hundreds of other salts, some of which are of great economic importance: *e.g.*, calcium carbonate, which occurs as limestone, marble, chalk, and coral. Magnesium carbonate also occurs in very large quantity, and when associated with calcium

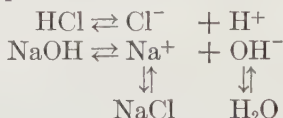
carbonate, the rock is known as dolomite, or magnesian limestone, a valuable building material. When limestones are heated, they lose carbon dioxide, leaving lime and magnesia, which are basic oxides of prime importance in industry. The earth's crust is composed largely of silicates.

246. Neutralization. — Acids and bases have very different chemical properties, and they readily interact to form salts. This is known as *neutralization*:



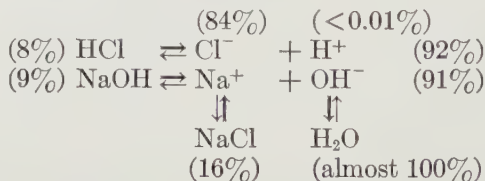
36.5 g. of HCl always unite with 40 g. of NaOH to form 58.5 g. of NaCl and 18 g. of water. By exactly neutralizing a solution of sodium hydroxide with hydrochloric acid, salt may be obtained by evaporation of the water.

From the standpoint of the ionic theory, the following example may be taken as a typical one:



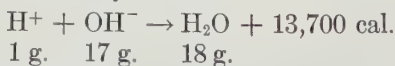
NaCl is formed, most of which is ionized. Hydrogen-ion unites almost completely with hydroxide-ion to form molecules of water.

A more detailed general plan for neutralization may be formulated as given below. For the interaction of 0.1 *N* hydrochloric and 0.1 *N* sodium hydroxide we have (235):



NaCl is 84 per cent ionized in 0.1 *N* solution, *i.e.*, there are 84 per cent of ions and 16 per cent of molecules. We also may observe that the percentage of H^+ and OH^- from the dissociation of H_2O is negligible (less than 0.01 per cent).

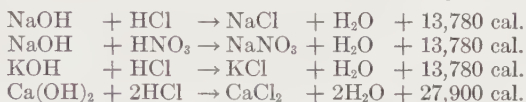
Neutralization, then, is essentially the combination of hydrogen-ion with hydroxide-ion to form water:



13,700 calories is called the *heat of neutralization*.

This view of neutralization is confirmed; for when an equivalent weight of a strong acid unites with an equivalent weight of a strong base to form 18 g. of water, the heat of neutralization is always the same (approximately 13,700 cal.).

Julius Thomsen, the Danish chemist, has measured many heats of reactions. Below are given a few heats of neutralization obtained by him:



With weak acids and bases the heat of neutralization may be either greater or less than that obtained in the case of strong electrolytes.

247. Neutralization and Volumetric Analysis. — Neutralization, as we have seen, gives rise to the formation of a salt along with water, and it presupposes a perfectly definite ratio between the base and the acid. The most important application of this is to the determination of the concentration of acids and bases. This requires *standard solutions*, or solutions of known concentration. The method of chemical measurement with standard solutions is known as **volumetric analysis**.

To understand neutralization as it relates to volumetric analysis, it is first necessary to have a clear conception of what is meant by a **normal solution**. The following is a general definition: *A normal solution contains one gram-equivalent of the active substance in a liter.* The equivalent weight in grams is known as a gram-equivalent.

A normal solution of a base (alkali) or of an acid contains one equivalent weight (gram-equivalent) of the base or of the acid in one liter of the solution. *One liter of a normal alkali contains 17 g. (approximately) of available hydroxyl, and one liter of normal acid contains 1 g. (approximately) of available hydrogen* (Review 165).

In determining the strength of an acid of unknown quantity, it is titrated with a standard solution of an alkali. The concentration of a base, on the other hand, is determined by titrating a given volume of it with a standard acid.

The analysis of sulfuric acid may be carried out as follows: A burette (Fig. 98) is filled with the standard alkali, *e.g.*, NaOH, and by means of a pipette exactly 25 cc. (or any other convenient volume) of the acid are introduced into a clean beaker, and then diluted with 8–10 volumes of water. A few drops of an alcoholic solution of phenolphthalein (an indicator which

is colorless with acids, but pink with slight excess of an alkali) are added, and the standard alkali run in drop by drop with constant stirring until a permanent pink tinge just appears. The volume of the alkali employed is now recorded.

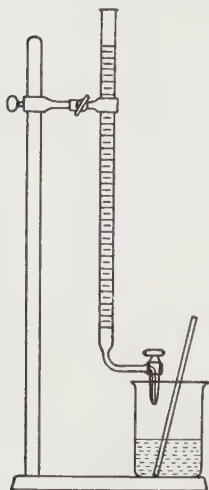
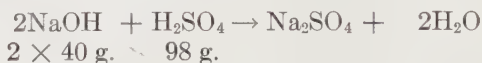


FIG. 98.

If 45 cc. of normal sodium hydroxide solution were required to neutralize 25 cc. of sulfuric acid, what would be the normal strength of the acid and its concentration in grams per liter?



The normal strength of the acid = $\frac{45}{25} = 1.8 \text{ N}$, *i.e.*, the acid is 1.8 times as strong as the alkali.

A normal solution of sodium hydroxide contains 40 g. of NaOH per liter, and a normal solution of sulfuric acid contains 49 g. of H_2SO_4 (see equation; also 165). $49 \times 1.8 = 88.2$ g. of H_2SO_4 per liter.

Such analysis of an acid is called **acidimetry**, and the corresponding analysis of an alkali, **alkalimetry**. The operation of analysis is called **titration**, and is very rapidly performed.

248. Indicators. — An indicator is employed in volumetric analysis to detect the end-point (condition of neutrality).

Indicators assume a decided color in the presence of a very slight excess of an acid or base, or turn sharply from one color to another. Some of the most common indicators are the following:

Indicator	Color with Bases	Color with Acids
Litmus.....	Blue	Red
Phenolphthalein.....	Purple-red	Colorless
Methyl orange.....	Yellow	Red
Congo red.....	Red	Blue

Different degrees of sensitiveness are shown by the indicators employed in testing acids and alkalies. Indicators also differ in their behavior with respect to mineral and organic acids.

Litmus solution, in the absence of carbonic acid, is a very good indicator for alkalies; it may also be employed as an indicator for such acids as sulfuric, nitric, hydrochloric, and oxalic.

Phenolphthalein is soluble in 50 per cent alcohol. Its neutral or acid solution is colorless. In the presence of faint excess

of a caustic alkali, phenolphthalein gives a fine purple-red. It may be used in titrating the hydroxides of the alkali and alkaline earth metals, except ammonium hydroxide; also with the mineral acids, and with acetic, oxalic, and other organic acids.

Methyl orange is a complex carbon compound which possesses a bright orange-red color and is readily soluble in water. It may be used as an indicator for the alkalies, including ammonium hydroxide, and for the mineral acids. It gives a yellow color with bases and a red color with acids. Methyl orange is very serviceable in the analysis of such carbonates as Na_2CO_3 and CaCO_3 , since the liberated carbonic acid has virtually no effect upon this indicator.

Congo red is the sodium salt of a complex organic acid. This indicator is red in neutral or alkaline solution, but is blue in the presence of acids (see Litmus). While litmus paper is equally red with all acids except the very feeblest, paper dipped in congo red exhibits gradations in color when brought in contact with acids of different strengths.

249. Classes of Salts. — There are several classes of salts:

(I) **Neutral or Normal Salts:** *e.g.*, KNO_3 , Na_2SO_4 , and $\text{Na}(\text{C}_2\text{H}_3\text{O}_2)$. These salts contain no available (ionizable) hydrogen in the molecule. Sodium acetate belongs to this class, because it is the salt of a monobasic acid:



A monobasic acid interacts with a base to form a neutral salt. It should be noted that "neutral salt" has no relation to the action of solutions of the salts on indicators.

(II) **Acid Salts:** *e.g.*, NaHCO_3 , KHSO_4 , Na_2HPO_4 . Acid salts contain available (ionizable) hydrogen:



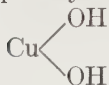
A dibasic acid (242) forms with each metal or base two salts — an acid salt and a neutral salt:



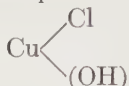
It requires two mols of KOH completely to neutralize one mol of sulfuric acid. Similarly, phosphoric acid forms three salts with an alkali or base.

(III) **Basic Salts.** Salts belonging to this class contain one or more hydroxyl radicals in the molecule: *e.g.*, $\text{Cu}(\text{OH})\text{Cl}$ (basic cupric chloride). This salt is half base:

Cupric hydroxide



Basic cupric chloride



Cupric chloride



Another basic salt is basic lead carbonate, or "white lead," $\text{Pb}_3(\text{OH})_2(\text{CO}_3)_2$; it is the basis of a very important paint.

(IV) **Mixed Salts.** Molecules of these salts contain mixed radicals, — either positive or negative: *e.g.*, NaKCO_3 , $\text{CaCl}(\text{OCl})$, $\text{KNa}(\text{C}_4\text{H}_4\text{O}_6)$, potassium-sodium tartrate (Rochelle salt).

(V) **Double Salts:** *e.g.*, $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ (alum) and $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ (Mohr's salt).

250. **Nomenclature of Acids and Salts.** — Review section (134).

The following examples illustrate how salts derived from polybasic acids are named:

Carbonic
acid



$\left\{ \begin{array}{l} \text{NaHCO}_3, \text{ Acid sodium carbonate, or Sodium bi-} \\ \text{carbonate} \\ \text{Na}_2\text{CO}_3, \text{ Sodium carbonate} \end{array} \right.$

Phosphoric
acid



$\left\{ \begin{array}{l} \text{NaH}_2\text{PO}_4, \text{ Primary sodium phosphate, or Sodium} \\ \text{dihydrogen phosphate} \\ \text{Na}_2\text{HPO}_4, \text{ Secondary sodium phosphate, or Di-} \\ \text{sodium hydrogen phosphate} \\ \text{Na}_3\text{PO}_4, \text{ Tertiary sodium phosphate, or Sodium} \\ \text{phosphate} \end{array} \right.$

The primary and secondary salts of phosphoric acid are acid salts.

251. **Formation of Salts.** — Salts may be formed in many different ways. The principal methods are as follows:

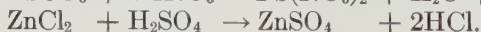
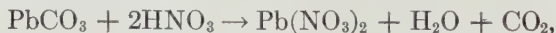
(1) *By synthesis:* $\text{Fe} + \text{S} \rightarrow \text{FeS}$.

(2) *By displacement:* $\text{Fe} + \text{H}_2\text{SO}_4 \rightarrow \text{FeSO}_4 + \text{H}_2$.

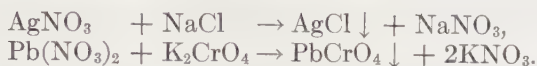
(3) *By the interaction of an oxide or hydroxide of a metal and an acid:*



(4) *By the interaction of a salt and an acid:*



(5) *By the interaction of solutions of salts (double decomposition):*



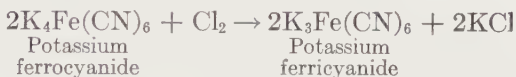
(6) *By the combination of a basic oxide and an anhydride:*



(7) *By the reduction of a salt:*

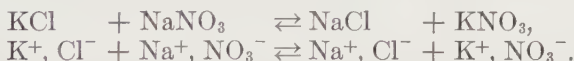


(8) *By the oxidation of a salt:*



(Why is this action regarded as oxidation?)

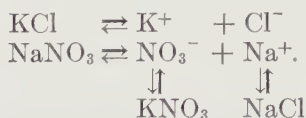
252. Double Decomposition in Solution. — When dilute aqueous solutions of potassium chloride and sodium nitrate are mixed, no very decided chemical change occurs, for the two salts tend to interact by double decomposition to form two other salts, both of which are quite soluble and are highly ionized:



This is an illustration of **Hess' law of thermoneutrality**: When dilute aqueous solutions of salts are mixed, there is practically no thermal effect, provided that no precipitation occurs.

This law has been known since about 1840.

In the example given above, we have four kinds of molecules and four different ions in equilibrium:



In case the solutions are quite dilute, the salts will be almost completely ionized; that is, the molecular concentrations will be very low.

The interaction of ferric chloride and ammonium thiocyanate (211) is another good illustration of double decomposition involving four soluble salts. Formulate this reaction in terms of ions.

253. Precipitation. — We have seen that, when aqueous solutions of silver nitrate and sodium chloride are mixed in the proper

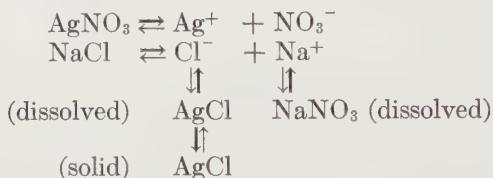
proportions, the reaction goes practically to completion, for insoluble silver chloride is formed:



The essential change is the union of Ag^+ and Cl^- to form a precipitate of AgCl .

In general, when two ionized substances are mixed, the action may be carried to completion in case one of the products is an insoluble substance.

The following plan may be followed in the formulation of reactions of this type:



Note the number of equilibria. Since AgCl is practically insoluble in water, a very slight excess of NaCl will effect complete precipitation.

If the least soluble of the four salts taking part in double decomposition is fairly soluble, strong solutions must be employed to effect even incomplete precipitation. This may be illustrated by mixing solutions of potassium bromide and sodium chlorate:



Potassium chlorate is much less soluble in water than are the other three salts, 6.6 g. dissolving in 100 cc. of water at 18° . This salt can be, therefore, only partially precipitated.

In certain cases two soluble salts interact to form two insoluble salts:

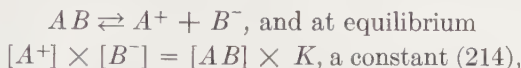


(Formulate this reaction from the standpoint of ions and equilibria.)

In any case of precipitation, it is the more complete the less the molecular solubility of the precipitate.

254. Solubility-Product. — When certain substances, such as salts, ionize in the presence of water (or other ionizing solvents), the action is reversible, the ionization continuing until a final state

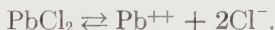
of equilibrium is established. Thus, when the salt AB ionizes we have —



the symbols in brackets standing for the molar concentrations of the ions and undissociated salt. Now let us assume that the temperature is constant, say, 18° , and that the undissociated salt is in equilibrium with the solid, or that the solution is saturated. For a saturated solution, we have

$$[A^+] \times [B^-] = \text{Constant},$$

for $[AB]$ is constant, and therefore $[AB] \times K$ must be constant. We may now state that *the product of the molar concentration of the ions is constant in a saturated solution of a substance at a given temperature.* The product $[A^+] \times [B^-]$ is known as the **solubility-product** of the substance AB . The product of the molar concentrations of the ions is also called the **ion-product constant**. The principle of the ion-product constant holds, in general, for difficultly soluble substances. In case the molecule dissociates into more than two ions, the ion concentrations must be raised to the power corresponding to the number of that kind of ion. For example, lead chloride ionizes thus:



For a saturated solution at a given temperature the solubility-product is $[\text{Pb}^{++}] \times [\text{Cl}^-]^2$.

Very slightly soluble substances, such as AgCl , BaSO_4 , and CaCO_3 , have very low solubility-products, while more soluble substances (*e.g.*, KClO_3 and NaCl) have higher. The value of the solubility-product varies, therefore, very greatly with different salts.

There are many applications of the principle of the solubility-product in chemistry. It is now easy to see why, when an excess of a solution of a chloride is added to a solution of a silver salt, the silver is practically all precipitated as AgCl . Silver chloride has a very low solubility-product, *i.e.*, it is almost insoluble in water. When the silver-ion and the chloride-ion come together, virtually all the ions unite to form AgCl , which is precipitated:



The product $[\text{Ag}^+] \times [\text{Cl}^-]$ is exceedingly low.

The principle makes it clear why an excess of the precipitant should be added. It also may be applied to the precipitation of barium as BaSO_4 , for this salt has a very low solubility-product. Again, we can readily understand the use of barium chloride and hydrogen chloride in the purification of rock salt. BaCl_2 removes the sulfates, for insoluble BaSO_4 is formed:



The ion-product constant $[\text{Ba}^{++}] \times [\text{SO}_4^{=}]$ is very low. When sufficient barium chloride is added to a solution of rock salt to remove the sulfates as BaSO_4 and the latter filtered off, the solution contains sodium chloride, together with certain impurities. When HCl is passed into the solution, NaCl is precipitated. Why is this the case? Sodium chloride has a fairly high solubility-product, *i.e.*, $[\text{Na}^+] \times [\text{Cl}^-] = \text{constant}$ is fairly large; but when HCl is passed into the solution, the concentration of the chloride-ion is greatly increased, due to the dissociation of HCl , so the value of $[\text{Na}^+] \times [\text{Cl}^-]$ is now no longer constant. As the solubility-product is exceeded, NaCl must separate out to restore equilibrium.

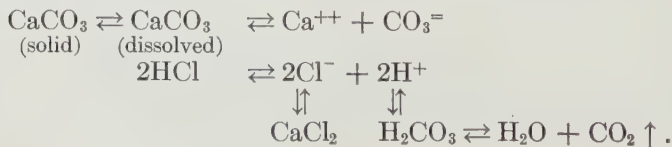
The following *experiment* may be carried out to illustrate solubility-product:

Prepare 100 cc. of a saturated solution of silver acetate, $\text{AgC}_2\text{H}_3\text{O}_2$ (about 1 g. of the salt at $20^\circ \text{C}.$), and then pour the solution into three test-tubes. Add to the first tube a small crystal of silver nitrate, AgNO_3 (not over 0.05 g.), and shake until the crystal dissolves. On allowing the solution to stand, a precipitate of silver acetate should be obtained. Explain.

Dissolve in the second tube a small crystal of sodium acetate, $\text{NaC}_2\text{H}_3\text{O}_2$, and explain the result.

Dissolve in the third tube a fairly large crystal of ammonium nitrate, NH_4NO_3 (must be free of chlorides), and note whether or not a precipitate is obtained. Explain.

255. The Formation of a Gaseous Substance. — When calcium carbonate is treated with hydrochloric acid in excess, the action runs to completion; for slightly ionized, unstable carbonic acid is formed, carbon dioxide escapes, and carbonate-ion is practically removed:



By the application of heat, all the CO_2 may be expelled. This reaction is typical of many others in which substances interact to form a gas, which may escape from the solution, thus removing some of the ions.

Substances may be removed from solution in two ways — (1) by precipitation and (2) as gases. In removing gases from solution advantage may be taken of Henry's law. The mass solubility of a gas, *i.e.*, the number of grams in solution per unit volume, is less under lower pressures; or, as a rule the molar solubility of a gas is directly proportional to its partial pressure. During the evolution of a gas its partial pressure may be kept down by blowing air or other indifferent gases through the solution. Such gases as CO_2 and H_2S may be completely removed from solution by this method.

Gases are more soluble in cold solvents than in hot; therefore many gases may be expelled completely by heating their solutions: for example, O_2 , N_2 , CO_2 , and H_2S . In this case the steam produced lowers the partial pressure of the gas, the steam taking the place of the current of air or indifferent gas.

256. Slightly Ionized Products; Repression of Ionization. — In the formation of NaCl from HCl and NaOH , one of the products (water) is very slightly ionized; hence the reaction goes practically to completion.

In general, if two highly ionized substances interact to form one highly ionized substance and one slightly ionized substance, the reaction will go practically to completion. The interaction of sodium hydroxide and ammonium chloride is a good illustration of this principle:



(Formulate this reaction from the ionic standpoint. Apply the principle also to the interaction of sodium acetate and hydrochloric acid.)

The ionization of a slightly ionized substance may be repressed by adding to its solution a substance capable of a high degree of ionization and having a common ion. Thus, when NH_4Cl (a highly ionized salt) is added to a solution of ammonium hydroxide (a weak base), more molecules of NH_4OH are formed, due to the increased concentration of the ammonium ion:



This means that the high concentration of NH_4^+ represses the

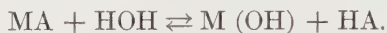
dissociation of NH_4OH . This may be illustrated by the following *experiment*:

A few drops of a solution of phenolphthalein are added to some very dilute ammonium hydroxide. A deep purple-red color indicates the presence of the hydroxide-ion (OH^-). When NH_4Cl is added to the liquid, the color disappears.

(Explain the effect of adding sodium acetate to acetic acid.)

This is another application of the common ion law; it is a very important principle (254).

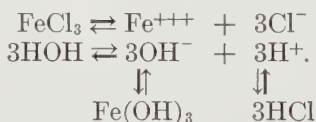
257. Hydrolysis of Salts. — Many soluble salts interact more or less with water, forming a base and an acid:



This reaction is typical of a chemical change called **hydrolysis**. In this particular change hydrolysis is the converse of neutralization. Water is a neutral substance and very feebly ionized, but all substances dissolved in water come under the influence both of hydrogen and hydroxide ions.

Hydrolysis will be considered under four heads:

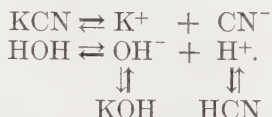
(1) **Salts of strong acids with weak bases.** When such salts as FeCl_3 , AlCl_3 , $\text{Bi}(\text{NO}_3)_3$, and $\text{Al}_2(\text{SO}_4)_3$ are dissolved in water, the solutions are strongly acidic; for the salts have a strong tendency to undergo double decomposition with water, *i.e.*, they are partially hydrolyzed. The interaction of FeCl_3 with water may be formulated thus:



Water is only slightly ionized, but as the hydroxide-ion combines with the ferric-ion to form slightly ionized $\text{Fe}(\text{OH})_3$, it (OH^-) is removed from the sphere of action, thus allowing more H_2O to dissociate to restore equilibrium. The concentration of the hydrogen-ion increases as hydrolysis proceeds; consequently, the solution may become strongly acidic. *In general, solutions of salts of strong acids with weak bases hydrolyze, giving a strongly acidic reaction.*

(2) **Salts of a strong base with a weak acid.** As is well known, aqueous solutions of such salts as KCN , Na_2CO_3 , Na_2S , and $\text{Na}_2\text{B}_4\text{O}_7$ (borax) are decidedly alkaline. A solution of potassium

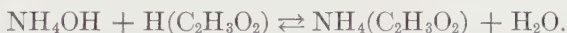
cyanide is strongly alkaline, for it hydrolyzes to form KOH, which is highly ionized. Hydrocyanic acid (HCN) also is formed, but is only feebly ionized:



In case of a 0.1 *N* solution of KCN at 25°, 1.12 per cent of the salt is hydrolyzed, while a solution of Na₂CO₃ is 3.17 per cent hydrolyzed.

We shall learn that soaps are salts belonging to this class; therefore, when they are treated with water, free alkali is formed, which no doubt takes some part in the cleansing action of these compounds. *In general, solutions of salts of strong bases with weak acids are strongly alkaline.*

(3) **Salts of a weak base with a weak acid.** This class of salts is represented by ammonium acetate, NH₄(C₂H₃O₂). In this particular case the base and acid are only moderately weak, and they react as follows:



This reaction does not run to completion as is the case when a strong acid is added to a strong base; it reaches equilibrium when a few tenths of 1 per cent of the free un-ionized base and free un-ionized acid are still in the solution.

Salts of feeble bases with feeble acids, in aqueous solution, are much more highly hydrolyzed than is ammonium acetate; indeed, such salts cannot be formed in the "wet way," *i.e.*, in the presence of water: *e.g.*, Al₂S₃.

In order to notice an effect when a salt is dissolved in water, the base and the acid must be of unequal activity.

(4) **Salts of strong bases with strong acids.** NaCl, KNO₃, and CaSO₄ belong to this class of salts. Solutions of such salts are neutral to indicators. In dilute solution the ionization of these salts, as well as that of the bases and acids from which they are derived, is generally complete, or practically so. In case the ionization is not quite complete, it will occur to practically the same extent for salt, base, and acid; consequently only very small, and equal, amounts of the ions H⁺ and OH⁻ are removed to form un-ionized base and acid. This upsets the equilibrium, which is restored by ionization of more water. The final result is that the

concentration of H^+ and OH^- is the same as in pure water; that is, the solution is neutral. In case, then, of very slight hydrolysis, the extremely small amounts of strong base and of strong acid which are formed, exactly neutralize one another.

258. Summary and Supplementary. —

(1) The qualitative reactions of such substances as KCl and $KClO_3$ can best be explained by assuming the existence of ions. KCl , like other chlorides, furnishes the chloride-ion (Cl^-) which combines with Ag^+ to form a precipitate of $AgCl$. On the other hand, chlorates ionize to form the chlorate-ion (ClO_3^-) and are not precipitated by the addition of silver nitrate. Neutralization is also satisfactorily explained by the ionization theory. In quantitative analysis complete precipitation is accomplished by adding the reagents in excess. This can be explained by the ionic theory (see "Solubility-Product").

(2) The abnormal freezing point depressions of electrolytes can be explained by assuming that molecules ionize to yield a larger number of particles.

(3) The conductivity of electrolytes, as well as electrolysis, are satisfactorily explained in terms of the ionization theory.

(4) The color of solutions of certain substances, *e.g.*, all permanganates, is explained by assuming the existence of a common colored ion.

(5) The Law of Mass Action (215) is applicable to weak electrolytes, such as acetic acid and ammonium hydroxide. Since their molecular conductivities are relatively small, it is assumed that their ionic concentrations are low, *i.e.*, weak electrolytes are not highly ionized. The equilibria, therefore, of solutions of weak electrolytes can be expressed by the law of mass action.

The equilibria in solutions of strong electrolytes, on the other hand, cannot be expressed by the law of mass action. We have, then, what is called the "anomaly of strong electrolytes." In other words, the theory of ionization as originally propounded and developed by Arrhenius and others does not fully explain or conform to all the known facts. This anomaly has furnished one of the strongest arguments against the theory of ionization.

The following illustration will show how the *anomaly of strong electrolytes* arises.

We have seen that for acetic acid (a weak electrolyte) the ionization constant K may be expressed as follows:

$$\frac{[H^+] \times [C_2H_3O_2^-]}{[H(C_2H_3O_2)]} = K_{\text{ionization}}$$

The numerical value of K was found to be approximately 0.000018 for a 0.1 N ($=0.1$ molar) solution of acetic acid at 18° . This value has been found by experiment for other concentrations of acetic acid, showing that the ratio $[H^+] \times [C_2H_3O_2]/[H(C_2H_3O_2)]$ is really constant, and that the ionization of acetic acid obeys the law of mass action or chemical equilibrium.

When the law of mass action is applied to a solution of sodium chloride we arrive at the expression:

$$\frac{[Na^+] \times [Cl^-]}{[NaCl]} = K_{\text{ionization}}$$

When the values obtained by experiment for different concentrations of NaCl are substituted in the above formula, a constant is not obtained, but wide divergences are found. Sodium chloride is a strong electrolyte, and is assumed to be highly ionized in dilute solution. Most other salts, as well as inorganic acids and bases, such as HCl, HNO_3 , NaOH, and KOH, show this anomaly.

Various attempts have been made to explain the "anomaly of strong electrolytes," none of which is entirely satisfactory. Debye¹ and Hückel have recently attempted to show that the theory of partial dissociation is incorrect. The analysis of solid salt crystals by the X-ray method has shown that such solids as NaCl and KCl are wholly ionic (64); therefore, it may be assumed that in solution, with the ions separated by the molecules of the solvent, complete dissociation or ionization of such substances is probable. If this be true, the original assumptions of Arrhenius that the conductance ratio is a measure of ionization must give way to newer postulates.

It may be assumed that in case of dilute solutions of strong electrolytes dissociation is practically complete, and any departures from the laws of ideal solutions may be attributed primarily to electrical forces between the ions. This inter-atomic attraction is assumed to affect the "activity" of any single ion, so the "activity" of any single ion depends upon the density of its "ionic atmosphere."

In the case of more concentrated solutions, the specific deviations which are observed may be ascribed principally to two factors:

- (1) The volume occupied by the ions under consideration; and
- (2) The interaction between the ions and the solvent.

The subjects of "strong electrolytes" and of "concentrated solutions" are still under investigation, and at present it is impossible to predict what the final outcome will be.

EXERCISES

1. Define and illustrate the following terms: acid; base; salt; neutralization; basicity of acid; and acidity of base.
2. Define and illustrate the following terms: neutral salt; acid salt; basic salt; mixed salt; double salt.

¹ Taylor's Elementary Physical Chemistry, p. 428.

3. What class of salts is illustrated by ordinary alum? How may the salt be prepared? Show how it ionizes.

4. Complete and balance the following equations, and write down the names of the various substances:

- (1) $\text{Ba}(\text{OH})_2 + \text{HNO}_3 \rightarrow$
- (2) $\text{Ca}(\text{OH})_2 + \text{H}_3\text{PO}_4 \rightarrow$
- (3) $(\text{NH}_4)\text{OH} + \text{H}_2\text{SO}_3 \rightarrow$
- (4) $\text{Fe}(\text{OH})_3 + \text{H}_2\text{SO}_4 \rightarrow$
- (5) $\text{KOH} + \text{H}_3\text{PO}_4 \rightarrow$

5. Write ionic equations to show the interaction of aqueous solutions of the following pairs of substances:

- (1) Sodium hydroxide + Nitric acid \rightarrow
- (2) Strontium hydroxide + Acetic acid \rightarrow
- (3) Zinc carbonate + Sulfuric acid \rightarrow
- (4) Silver nitrate + Potassium chlorate \rightarrow
- (5) Silver acetate + Potassium chloride \rightarrow

6. What important conclusion may be drawn from the fact that the heat of neutralization of equivalent quantities of strong acids and bases is practically constant? State and illustrate Hess' law of thermoneutrality.

7. Show how polybasic acids (*e.g.*, H_2CO_3 and H_3AsO_4) may ionize.

8. Explain why the electrolysis of dilute sulfuric acid yields oxygen at the anode, while the electrolysis of rather concentrated sulfuric acid (say, 50 per cent) yields persulfuric acid ($\text{H}_2\text{S}_2\text{O}_8$).

9. If 42.5 cc. of a solution of 0.5 *N* hydroxide were required to neutralize 25 cc. of an unknown acid solution, find the normality of the acid. If the acid were sulfuric, how many grams of H_2SO_4 would there be in a liter of it?

10. A liter of a solution contains 2.65 g. of pure anhydrous sodium carbonate. 10 cc. of this solution are withdrawn, diluted with water, a few drops of a solution of the indicator methyl orange added, and the solution finally titrated with 0.2 *N* hydrochloric acid. Find the volume of acid required.

11. Write the names and formulae for all the possible ammonium and calcium salts of phosphoric acid.

12. (a) Explain and also illustrate, in terms of the ionic theory, the following: A strong acid; a weak acid; a feeble acid; a strong base; a weak base.

(b) In accordance with these terms, classify the following: HBr , $\text{Ba}(\text{OH})_2$, H_2S , $(\text{NH}_4)\text{OH}$, NaOH , H_2CO_3 , H_2SO_4 .

13. (a) What weight of available hydrogen is present per cubic centimeter in 0.5 *N* phosphoric acid?

(b) What volume of hydrogen at S.T.P. could be obtained by treating 30 cc. of 0.5 *N* phosphoric acid with an excess of magnesium?

14. A solution of barium hydroxide contains 4.275 g. of the compound per liter. How many cc. of 0.1 *N* sulfuric acid are required to precipitate all the barium contained in 635 cc. of the solution?

15. Explain from the standpoint of the theory of ionization and chemical equilibrium:

- (a) The interaction of a solution of barium chloride and sulfuric acid;
- (b) The solubility of ferrous sulfide in acids;
- (c) The interaction of aqueous solutions of potassium chloride and sodium nitrate.

16. 100 g. of water at 18° dissolve 0.00023 g. of BaSO_4 . Find the molar solubility of the salt. Assuming that the salt, in the saturated solution, is completely ionized, calculate its solubility-product.

17. Show how the principle of the ion-product constant may be applied to the purification of common salt.

18. The molar solubility of silver acetate at 16°C. is 0.0603 and the fraction of the salt ionized is 0.71. Calculate the solubility-product of the salt.

19. 100 cc. of water at 18°C. dissolve 0.17 g. of calcium hydroxide. Assuming that the base is 90 per cent ionized, find its solubility-product.

20. If the molar solubility of the chloride of a certain bivalent metal is 0.05 at 18°C. , what is the solubility-product of the salt, assuming that it is 60 per cent ionized?

21. (a) How could you repress the ionization of $\text{H}(\text{C}_2\text{H}_3\text{O}_2)$ and of $\text{NH}_4(\text{OH})$?

(b) Why does aluminium sulfate destroy the alkalinity of soil?

22. Explain the chemical change, if any, when water is added separately to each of the following substances: CaS , AlCl_3 , Na_2SO_4 , K_2CO_3 , $\text{Na}(\text{C}_2\text{H}_3\text{O}_2)$, and $\text{Al}(\text{C}_2\text{H}_3\text{O}_2)_3$.

23. When a dilute solution of stannic chloride stands for some time, its electrical conductance gradually increases and finally becomes constant. Explain.

24. What is meant by the statement, "anomaly of strong electrolytes"? Summarize the evidence in favor of the Arrhenius theory of ionization; also state one or more objections to the theory.

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KOLTHOFF-FURMAN. Indicators.

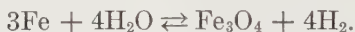
SCHLESINGER. General Chemistry, Chaps. XIII-XV.

STIEGLITZ. Qualitative Chemical Analysis, Part I.

CHAPTER XV

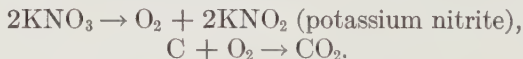
OXIDATION AND REDUCTION

In the study of oxygen it was pointed out that oxidation, in its narrowest meaning, is combination with oxygen. It has also been pointed out that reduction is the converse of oxidation, *i.e.*, the removal of oxygen from a substance:



In the reaction to the right, iron is oxidized and water reduced; in the opposing reaction, iron tetroxide is reduced and hydrogen is oxidized. Oxidation and reduction are therefore simultaneous and chemically equivalent. Thus, equivalents of hydrogen and oxygen unite to form water.

259. Oxidizing Agents. — We also have seen that various compounds part with oxygen more or less readily, and therefore act as oxidizing agents. Thus, when potassium nitrate is heated in a porcelain crucible, oxygen is liberated, and it will ignite particles of charcoal (carbon) when dropped into the crucible:



Some of the most important oxidizing agents are the following:

- (1) The Peroxides, — H_2O_2 , Na_2O_2 , BaO_2 , etc.
- (2) Certain Dioxides, such as MnO_2 and PbO_2 .
- (3) Nitric Acid (HNO_3) and Nitrates, — KNO_3 , NaNO_3 , etc.
- (4) Chlorates, — KClO_3 , $\text{Ba}(\text{ClO}_3)_2$, etc.
- (5) Hypochlorites, — NaClO , KClO .
- (6) Permanganates, — KMnO_4 , NaMnO_4 , etc.
- (7) Sulfuric Acid, H_2SO_4 .
- (8) Chromic Anhydride and Dichromates, — CrO_3 , $\text{K}_2\text{Cr}_2\text{O}_7$, $\text{Na}_2\text{Cr}_2\text{O}_7$.

Warning. *It is exceedingly dangerous to rub together in a mortar oxidizing agents and combustible materials. Likewise, great care must be exercised in heating certain oxidizing agents, particularly*

when they are mixed with combustible materials, such as carbon and sulfur.

Ordinary gunpowder is a mixture of sulfur, charcoal (carbon), and potassium nitrate. In this case we have an oxidizing agent mixed with two combustible materials; so when a gun is discharged, combustion is supported by oxygen liberated from potassium nitrate, and is not dependent upon the oxygen of the atmosphere. Large volumes of gases, such as CO_2 and SO_2 , are formed at a very high temperature; therefore the ball is projected from the gun with great velocity.

Potassium chlorate, when heated sufficiently, gives up all its oxygen, forming potassium chloride; it is a powerful oxidizing agent and as such is used in the manufacture of matches, fireworks, and explosives.

Concentrated sulfuric acid, especially when hot, is capable of oxidizing certain substances. Thus, sulfur may be oxidized to SO_2 :

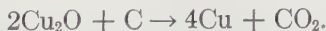


Potassium permanganate and concentrated sulfuric acid form a powerful oxidizing agent (113).

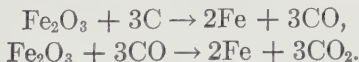
260. Reduction and Reducing Agents. — A reducing agent, as previously stated, robs a substance of oxygen. Some of the most important reducing agents are as follows:

- (1) Carbon, C (at high temperatures).
- (2) Carbon monoxide, CO (at high temperatures) and sulfur dioxide, SO_2 .
- (3) Hydrogen and Water Gas ($\text{H}_2 + \text{CO}$).
- (4) Certain Hydrogen Compounds, — H_2S , HI, H_2SO_3 , etc.
- (5) Certain Metals, — Al, Na, K, Mg, etc. (at high temperatures).
- (6) Ferrous Compounds, — FeO, FeSO_4 , etc.

Carbon (coke, charcoal) and carbon monoxide are the most important reducing agents in liberating the metals from their ores or oxides. Thus, cuprite (cuprous oxide), Cu_2O , is an ore of copper. It may be reduced by heating with carbon:



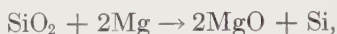
Our most important iron ore is hematite, Fe_2O_3 . It is reduced in a blast furnace by means of carbon and carbon monoxide:



Zinc oxide, ZnO , is also reduced by means of carbon:



Magnesium reduces SiO_2 , and aluminium reduces such oxides as Cr_2O_3 , Fe_2O_3 , and MnO_2 :



These reductions take place at very high temperatures.

261. A Broader Definition of Oxidation and Reduction. — Thus far we have used the terms oxidation and reduction in the simplest or narrowest sense. They are used, however, in a much wider sense, and may be defined as follows:

Oxidation is the chemical combination of oxygen or any other acid-forming (non-metallic) element or radical with a substance, or the removal of hydrogen or any basic (metallic) element or radical. Reduction is the converse.

Thus, when ferrous chloride is treated with chlorine, it is oxidized to ferric chloride:

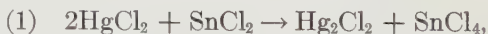


Again, concentrated sulfuric acid oxidizes hydrogen bromide to free bromine:



HBr is oxidized because it loses hydrogen, and H_2SO_4 is reduced to unstable sulfurous acid, H_2SO_3 .

Stannous chloride may reduce mercuric chloride to mercurous chloride or mercury:



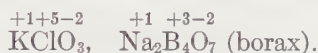
Stannous chloride is oxidized to stannic chloride.

When HgCl_2 is in excess, Hg_2Cl_2 is obtained as a white precipitate; but when an excess of SnCl_2 is used, the chloride is reduced to metallic mercury, giving a dark precipitate.

262. Oxidation and Reduction and Valence. — A compound is composed of elements which are, relatively to one another, either positive or negative. Thus, in CuO , copper is positive and oxygen negative; in CO_2 , carbon is positive as related to oxygen; in

PCl_5 , P is positive and Cl negative, but in PH_3 (or H_3P) H is positive and P negative.

The sum of the positive and negative valences of an element does not exceed 8 (89). Thus, chlorine has a maximum positive valence of 7 (Cl_2O_7) and a minimum negative valence of 1 (HCl). In writing formulae for compounds it should be remembered that *the algebraic sum of the positive and negative valences is zero*:

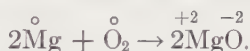


In the case of borax the sum of the valences is $(2 + 12) - 14 = 0$.

Oxidation and reduction are sometimes defined as follows:

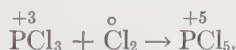
“Oxidation consists in increasing the active valence of a positive element, or decreasing that of a negative element. Reduction is the converse.”

Thus, when magnesium is oxidized to magnesium oxide, we have:

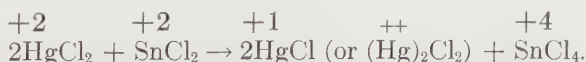


In MgO magnesium and oxygen have an active valence of 2, but in the elementary state they have no active valence.

Likewise, when PCl_3 is transformed into PCl_5 , the active valence of P increases to 5:



Again, when HgCl_2 is reduced to Hg_2Cl_2 , the active valence of Hg is reduced from 2 to 1:

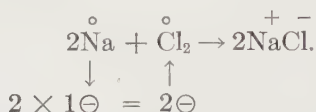


At the same time, the active valence of Sn is increased from 2 to 4. In other words, HgCl_2 is reduced and SnCl_2 is oxidized.

The following series of compounds illustrate the change of valence accompanying oxidation:

Ferrous Compounds	Ferric Compounds	Stannous Compounds	Stannic Compounds
$\overset{+2}{\text{FeO}}$	$\overset{+3}{\text{Fe}_2\text{O}_3}$	$\overset{+2}{\text{SnO}}$	$\overset{+4}{\text{SnO}_2}$
$\text{Fe}(\text{OH})_2$	$\text{Fe}(\text{OH})_3$	$\text{Sn}(\text{OH})_2$	$\text{Sn}(\text{OH})_4$
FeCl_2	FeCl_3	SnCl_2	SnCl_4
$\text{Fe}(\text{NO}_3)_2$	$\text{Fe}(\text{NO}_3)_3$	SnS	SnS_2
FeSO_4	$\text{Fe}_2(\text{SO}_4)_3$	$\text{Sn}(\text{NO}_3)_2$	$\text{Sn}(\text{NO}_3)_4$

263. **Oxidation and Reduction and Electrons.** — It has been stated that oxidation may be regarded as the loss of electrons by an atom or group of atoms, while reduction is the converse. Let us take the very simple illustration of the formation of sodium chloride by the direct combination of its constituents. The reaction may be formulated thus:



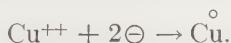
Electrons are no doubt transferred from the sodium to the chlorine atoms, the change being accompanied by the evolution of energy. Examination of crystals of sodium chloride by modern methods (64) shows that the compound is ionized (at least potentially so); and when salt is dissolved in water the ions serve as transports for electricity, as, for example, during electrolysis. Sodium is strongly electropositive and chlorine strongly electronegative, thus giving rise to a polar compound (88). The sodium atom is oxidized and the chlorine atom is reduced. We therefore have an experimental basis for assuming that in the synthesis of salt there is actually a transference of electrons.

In general, chemical reactions, such as the oxidation-reduction reaction, can be explained by assuming either the transference of electrons from atoms to other atoms in the reacting systems, or, in certain cases, to rearrangements of the electrons in some of the electron orbits or shells (132). The oxidation-reduction reaction is therefore closely connected with the transference and rearrangement of electrons. In the combination of sodium and chlorine to form salt, there is a direct transference of electrons, giving rise to what is termed "electro-valence," the atoms or ions being held together by electrostatic forces.

We may regard electrolysis as an oxidation-reduction reaction, oxidation occurring at the anode and reduction at the cathode. In other words, electrons are lost by ions at the anode and gained by ions at the cathode. Thus, when a halide is subjected to electrolysis, the halogen is liberated at the anode: e.g., when hydrochloric acid is electrolyzed, chlorine is obtained:



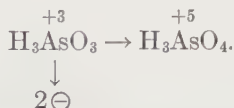
When an electric current is passed through a solution of a salt, such as CuSO_4 , the electrochemical change at the cathode is regarded as reduction, for electrons are gained by the ions:



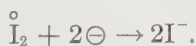
This is the kind of reaction involved in electroplating.

The use of the electric current in oxidation and reduction will be considered at greater length in a subsequent chapter (see Electrochemistry, Chap. XXXIV).

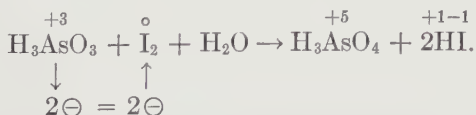
264. Balancing Equations by the "Valence Change" Method. — Under the heading entitled "Oxidation and Reduction and Electrons" it was shown how a simple equation may be balanced by the "electron" or "valence change" method. It also may be illustrated by oxidizing arsenious acid to arsenic acid. This may be done by titrating a solution of the former with a standard iodine solution, starch being used as indicator. In changing from arsenious acid to arsenic acid, the trivalent arsenic atom is regarded as losing two electrons (oxidation), which raises the valence of arsenic to +5:¹



The two electrons lost by an atom of arsenic are capable of reducing a molecule of iodine to iodide ions:



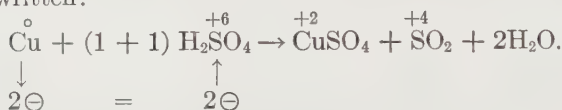
The reaction is carried out in aqueous solution, and we may consider that iodine interacts with water, forming oxygen, which transforms arsenious acid to arsenic acid. The complete change may now be summarized thus:



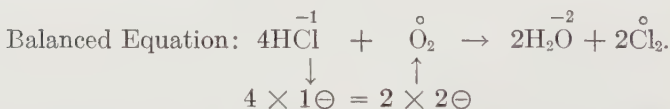
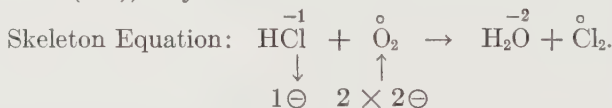
¹ In writing these equations the method employed by H. I. Schlesinger in his textbook entitled "General Chemistry" (Chap. XVIII) has been followed. In the opinion of the author nothing could be clearer or more condensed.

We have, then, the experimental fact that iodine oxidizes a solution of arsenious acid to arsenic acid, and have endeavored to explain it in terms of valence change and electrons.

Again, when copper is dissolved in hot concentrated sulfuric acid, copper sulfate, sulfur dioxide, and water are the products. In this reaction the valence of sulfur may be considered as changing from $+6(\overset{+6}{\text{H}_2\text{SO}_4})$ to $+4(\overset{+4}{\text{SO}_2})$, for which two electrons are required. These can be supplied by an atom of copper. At the same time CuSO_4 is formed. One copper atom is therefore capable of reducing one molecule of H_2SO_4 , and a second molecule of H_2SO_4 is required to form one molecule of CuSO_4 . The equation may now be written:

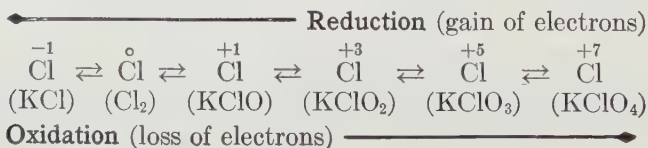


The equation for the reaction involved in the Deacon process for chlorine (271), may be written thus:



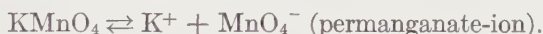
One molecule of oxygen is capable of oxidizing four molecules of hydrogen chloride, two molecules of chlorine being produced. By inspecting the equation it may be seen that each chlorine particle loses an electron, four of which are required to raise the active valence of two oxygen atoms from zero to -2 .

Modern chemical theory considers that atoms have "valence" electrons (88), and that chemical changes are due to the removal of electrons from atoms or to their addition to atoms. Chlorine is a multivalent element. In the series of changes indicated below, those to the right are regarded as oxidation, while those to the left are reduction:



265. Balancing Equations by the Ion-Electron Method.—Equations involving electrolytes, and therefore ions, can be balanced by what is known as the “ion-electron” method. Some writers and teachers prefer this method to the “valence change” method described in the previous section, while others think it is more complicated. For the balancing of molecular equations the “valence change” method is quite satisfactory, and is undoubtedly simpler than the “ion-electron” method. This latter method is based largely upon the fact that *most reactions involving electrolytes can be carried out so as to produce an electric current from them.*

The interaction of potassium permanganate and strong hydrochloric acid is an excellent illustration of this method. When potassium permanganate and hydrochloric acid interact, the molecular products are KCl, MnCl₂, Cl₂, and H₂O (271). When potassium permanganate is dissolved in water, it ionizes thus:



Since the potassium-ion is not affected during the reaction, the substances really concerned are as follows:



When hydrochloric acid acts upon potassium permanganate, the former is oxidized to free chlorine, and the latter is reduced, manganous chloride being formed. In terms of ions and electrons the changes may be represented thus:



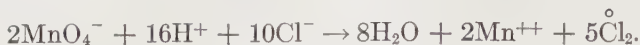
Each MnO_4^- interacts with 8H^+ to form $4\text{H}_2\text{O}$, and the one atom of manganese with a valence of +7 gains 5 electrons, the valence being reduced to +2 (Mn^{++}). The electrons are supplied by the chloride-ion (from HCl):



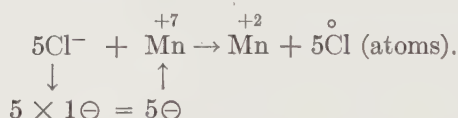
10 electrons and 16H^+ are capable of reducing 2MnO_4^- :



Summing up, we may now write:



The writing of the equation for the above reaction may be somewhat simplified by a combination of the "valence change" method and the "ion-electron" method, and has the additional advantage that we have in the end the *molecular equation*. The explanation is as follows: In potassium permanganate the valence of manganese is +7 while in manganous chloride it is reduced to +2. This change in valence requires 5 electrons, which may be supplied by 5 chloride ions from hydrochloric acid. The essential change may be simply expressed as follows:



In order to get elementary chlorine (Cl_2), 2 atoms of manganese are required, which means that 2 molecules of KMnO_4 must be used. It is now clear that 10Cl^- are required to reduce the two atoms of septivalent manganese. Since 2 molecules of KCl and 2 of MnCl_2 are formed, 6 more chloride ions are needed, making 16 in all. This means, of course, 16 molecules of HCl . The equation may now be balanced:



The production of an electric current by the oxidation-reduction reaction will be discussed in a subsequent chapter (XXXIV).

We thus see that the balancing of equations may take various forms. Before balancing any equation, it is necessary to know the names and formulae of the factors and products. The nature of the products is determined by experiment. It should always be remembered that equations for reactions must conform to the law of the conservation of mass, and they have an experimental basis. In applying the ion-electron method, it also should be kept in mind that electrons are neither created nor destroyed: they simply pass from atoms or groups of atoms to other atoms or groups

of atoms, and an electron lost by an atom is gained by some other atom.

Other oxidation-reduction reactions will be considered in detail further on, and particularly in connection with the halogens (Chap. XVI) and nitric acid (Chap. XXII).

EXERCISES

1. Define oxidation and reduction in the broadest sense, and illustrate by writing a number of equations.

2. Give the names and formulae of a number of the best oxidizing agents; also reducing agents.

3. Are the following statements satisfactory? Oxidation means an increase of positive valence, or a decrease of negative valence; reduction is the converse. Explain.

4. Justify the following statement: "When an oxidizing agent and a reducing agent interact, the total change in valence suffered by each is exactly the same, though opposite in direction."

5. Define oxidation and reduction in terms of electrons. Illustrate.

6. Balance the following skeleton equations by the "electron" method:

- (1) KNO_3 (heated) + $\text{C} \rightarrow \text{KNO}_2 + \text{CO}_2$,
- (2) $\text{H}_2\text{AsO}_3 + \text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{AsO}_4 + \text{HCl}$,
- (3) $\text{FeBr}_3 + \text{H}_2\text{S} \rightarrow \text{FeBr}_2 + \text{HCl} + \text{S}$,
- (4) $\text{Cu} + \text{HNO}_3 \rightarrow \text{Cu}(\text{NO}_3)_2 + \text{NO} + \text{H}_2\text{O}$,
- (5) $\text{Zn} + \text{H}_2\text{SO}_4$ (conc.) $\rightarrow \text{ZnSO}_4 + \text{H}_2\text{S} + \text{H}_2\text{O}$.

7. Balance the following skeleton equations by the "ion-electron" method:

- (1) $\text{K}_2\text{Cr}_2\text{O}_7 + \text{HCl} \rightarrow \text{KCl} + \text{CrCl}_3 + \text{H}_2\text{O} + \text{Cl}_2$,
- (2) $\text{KMnO}_4 + \text{FeSO}_4 + \text{H}_2\text{SO}_4 \rightarrow \text{K}_2\text{SO}_4 + \text{MnSO}_4 + \text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{O}$,
- (3) $\text{Na}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{Na}_2\text{SO}_4 + \text{Cr}_2(\text{SO}_4)_3 + \text{H}_2\text{O}$,
- (4) $\text{H}_2\text{S} + \text{I}_2 \rightarrow ?$
- (5) $\text{HgCl}_2 + \text{SnCl}_2 \rightarrow ?$

8. Express in words the significance of the following:

- (1) $\text{NO}_3^- + 2\text{H}^+ + \ominus \rightleftharpoons \text{NO}_2 + \text{H}_2\text{O}$,
- (2) $\text{NO}_3^- + 4\text{H}^+ + 3\ominus \rightleftharpoons \text{NO} + 2\text{H}_2\text{O}$,
- (3) $\text{NO}_3^- + 3\text{H}^+ + 2\ominus \rightleftharpoons \text{HNO}_2 + \text{H}_2\text{O}$,
- (4) $\text{MnO}_4^- + 8\text{H}^+ + 5\ominus \rightleftharpoons \text{Mn}^{++} + 4\text{H}_2\text{O}$,
- (5) $\text{Zn} + 2\text{H}^+ \rightleftharpoons \text{H}_2 + \text{Zn}^{++}$.

9. What volume of H_2S (S.T.P.) is needed to reduce 10 g. of $\text{K}_2\text{Cr}_2\text{O}_7$ in the presence of sulfuric acid, assuming that sulfur is one of the reduction products?

10. When silver is dissolved in concentrated sulfuric acid, sulfur dioxide is evolved. Write the equation for the reaction.

READINGS AND REFERENCES

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JETTE. Oxidation-Reduction Reactions.

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STIEGLITZ. Qualitative Chemical Analysis, Vol. I, Chap. XIV-XV.

CHAPTER XVI

THE HALOGENS

266. **Relationships and General Characteristics.** — The Seventh Group of the Periodic Table contains five well-known elements, four of which constitute a natural family called the **halogens** (Greek, meaning *salt-producers*). The names of these elements, together with their atomic numbers and atomic weights, are:

	At. No.	At. Wt.
Fluorine, F.	9	19.0
Chlorine, Cl.	17	35.46
Bromine, Br.	35	79.92
Iodine, I.	53	126.93

Manganese (688) and the recently discovered elements *masurium* and *renium* constitute Sub-group A of the seventh group. In most respects manganese is quite unlike the halogens; it is a metal, closely resembling iron and chromium in many of its properties.

Some of the *general characteristics of the halogen family* are given below.

There is a deepening in color as we pass from fluorine to iodine, fluorine being a pale greenish-yellow gas, while the vapor of iodine is violet.

The boiling points of the liquids and the melting points of the solids gradually increase with increasing atomic weight. Fluorine has the greatest volatility, *i.e.*, it is the most difficult to liquefy.

The density increases with increase in atomic weight, bromine and iodine being heavier than some of the metals.

The halogens are the most electronegative elements known, the electronegative character decreasing from fluorine through chlorine and bromine to iodine. This means that the halogens combine with the alkali metals (489) with the greatest readiness and with the display of much energy.

They all unite with hydrogen to form similar compounds. HF is the most stable and HI the least stable of these compounds. Hydrogen and fluorine unite most vigorously. Their hydrides are colorless gases (H_2F_2 boils at 19.4°) and very soluble in water,

forming acids. The *heats of formation* of these compounds are as follows:

HF.....	38,600 cal.
HCl.....	22,000 cal.
HBr.....	8,400 cal.
HI.....	-6,000 cal.

These heats of formation are indicative of the relative stabilities of the four compounds. HF is very stable and HI is fairly unstable. The affinity of fluorine is so great that it will unite with hydrogen in the dark. As is well known, HBr and HI are reducing agents.

The halogens unite with metals to form similar compounds known as *halides*: M^IX , $M^{II}X_2$, etc. The *heats of formation* of their potassium salts are:

KF.....	118,100 cal.
KCl.....	104,300 cal.
KBr.....	95,100 cal.
KI.....	80,100 cal.

Fluorine does not unite directly with gold or platinum, which are attacked by chlorine. Fluorine forms no oxygen compounds and iodine forms the most stable oxides. It is an extraordinary fact that the extremely electronegative fluorine atoms unite to form molecules (F_2), yet they are unable to combine with oxygen which approaches fluorine in electronegative character.

The halogens possess a multiple valence. As previously stated, the valence varies from -1 to $+7$. They are univalent (negative) with respect to hydrogen and the metals.

Chlorine, bromine, and iodine form *oxy-acids* of similar character, such as:

Hypochlorous acid.....	HClO
Chlorous acid.....	HClO ₂
Chloric acid.....	HClO ₃
Perchloric acid.....	HClO ₄

In general, the stability of the oxygen compounds of the halogens increases from chlorine to iodine. Thus, iodine is able to displace chlorine from chloric acid or chlorates:



Some of the halogens combine with each other forming compounds such as ICl, ICl_3 , and IBr.

The properties of the halogens are summarized in the table given below.

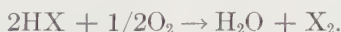
Property	Fluorine, F	Chlorine, Cl	Bromine, Br	Iodine, I
Atomic Weight.	19.0	35.46	79.92	126.93
State.....	Gas	Gas	Liquid	Solid
Boiling point...	-187°	-33.6°	+59°	+184°
Melting point..	-223°	-102°	-7°	+114°
Density.....	1.14 (liq.)	1.51 (liq.)	3.18 (liq.)	4.95 (solid)
Color.....	Pale greenish-yellow	Greenish-yellow	Red-brown	Dark gray
Hydrides, XH.	HF (H ₂ F ₂ , H _x F _x)	HCl	HBr	HI
Oxy-acids.....	HClO HClO ₂ HClO ₃	HBrO HBrO ₂ HBrO ₃	HIO HIO ₂ HIO ₃

267. Comparative Methods of Preparing the Halogens. —

The general methods for the preparation of the halogens are:

(I) *Oxidation of an aqueous solution of the hydracid (HX).*

In general, a halogen is liberated when a good oxidizing agent is treated with a strong solution of a hydracid: *e.g.*, when MnO₂ or KMnO₄ is treated with hydrochloric acid. In outline, the essential change may be expressed thus:



Fluorine, however, cannot be prepared by this method.

(II) *By the electrolysis of the halides under proper conditions.*

(III) *Decomposition of a perhalide by heat.* For example:

Cerium tetrafluoride (CeF₄) yields fluorine and a lower fluoride, and PbCl₄ dissociates into PbCl₂ and Cl₂.

268. **Occurrence of the Halogens.** — All four elements are very widely distributed in nature, and occur principally in the form of salts, such as NaCl, KCl, MgBr₂, and CaF₂. All the halogens also occur in vegetable and animal matter. According to J. H. L. Vogt, the earth's crust contains the following percentages:

Chlorine.....	0.175
Fluorine.....	0.025 to 0.04
Bromine.....	0.001
Iodine.....	0.0001

“Roughly, to every 1,000 parts by weight of chlorine present in the earth's crust, there occur 140 to 230 parts of fluorine, but only 6 parts of bromine and 0.6 part of iodine.” We thus see

that these elements constitute only a minor part of the earth's crust (18), particularly bromine and iodine.

In sea-water there are about 10 to 12 parts of bromine to 1 part of iodine, and 150 parts of chlorine to 1 part of bromine. As we shall see later, it is possible to extract bromine on a large scale from sea-water. There is very little fluorine in sea-water, although in the earth's crust it ranks next to chlorine.

In this connection it is interesting to note that manganese is very widely distributed in the earth's crust, of which it constitutes probably not over 0.08 per cent.

CHLORINE. Cl = 35.46.

269. History. — Scheele, in 1774, treated pyrolusite (MnO_2) with hydrochloric acid and liberated a greenish-yellow gas which bleached vegetable colors. He thought it was muriatic (Lat. *muria*, brine) acid deprived of phlogiston, and called it "dephlogisticated marine gas." Berthollet (1785) thought that the gas was a compound of muriatic acid and oxygen, or "oxymuriatic acid." Davy (1809-1818) established the elementary nature of the substance, and named it **chlorine** (Greek, *pale green*, or *greenish-yellow*).

270. Occurrence. — Chlorine does not occur in the free state, for it is too active. It occurs in large quantities as chlorides, — NaCl , KCl , and MgCl_2 being especially abundant, since they constitute the largest proportion of the solid matter in sea-water. Of the 3.6 per cent total solids in sea-water, about 2.8 per cent is NaCl . Large deposits of sodium chloride are also found as rock-salt. The salt beds of Stassfurt, Germany, contain large quantities of the chlorides of potassium and magnesium, as well as sodium. AgCl (horn-silver) is one of the ores of silver.

271. Preparation. — I. **By Electrolysis.**

Chlorine may be prepared by the electrolysis of fused chlorides or aqueous solutions of chlorides.

Thus, chlorine may be liberated by passing the current through fused NaCl , KCl , or AgCl . Very pure chlorine is prepared by the electrolysis of fused AgCl between carbon electrodes, the gas being liberated at the anode.

Chlorine also may be prepared by passing the current through a solution of HCl , NaCl , KCl , or other soluble chlorides.

In case hydrochloric acid is electrolyzed, equal volumes of hydrogen and of chlorine are liberated. When an aqueous solution of NaCl is subjected to electrolysis, hydrogen, chlorine, and sodium

hydroxide are formed. The sodium travels toward the cathode (negative electrode), but is not liberated. Instead of this, sodium hydroxide is formed and hydrogen escapes.

The electrolysis of sodium chloride may be shown by passing a current of electricity through a solution (Fig. 99). If a small quantity of a neutral solution of litmus is added, it is bleached around the anode and colored blue around the cathode. As chlorine is soluble in water, it is not noticeably released until the liquid around the anode is saturated with the gas.

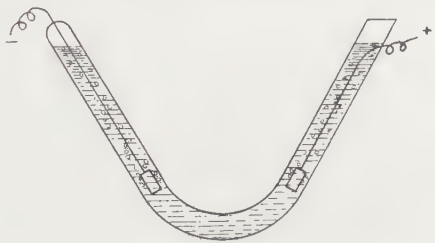


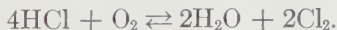
FIG. 99.

The greater part of the world's consumption of chlorine is produced by the electrolysis of aqueous solutions of the chlorides of sodium, potassium, and zinc, especially the two former.

We have seen that the electrolysis of sodium chloride yields hydrogen, sodium hydroxide, and chlorine. At first glance, the process appears to be rather simple, but there are serious obstacles to be overcome in all electrolytic processes for decomposing sodium chloride with the current. For example, if sodium hydroxide and chlorine come together, they will interact to form other substances. These substances are usually kept apart by separating the anode and cathode compartments of the electrolytic cell by means of a porous diaphragm. Various cells are in use, such as the Nelson and the Townsend. Anodes of carbon are employed (495).

II. By the Interaction of Hydrogen Chloride and Free Oxygen.

Chlorine may be prepared by the oxidation of hydrogen chloride by the oxygen of the air (**Deacon's Process**). This is accomplished in the presence of certain metallic salts (catalysts). Cupric chloride (CuCl_2) is particularly effective:



As the reaction is reversible, an equilibrium is established, so not all the HCl is decomposed. At a temperature of approximately 400° , about 84 per cent of the HCl is decomposed.

The formation of chlorine by this method may be shown by passing hydrogen chloride and oxygen over heated pumice stone

saturated with cupric chloride, as shown in Fig. 100. The pumice stone is first soaked in a solution of cupric chloride and then dried. By allowing oxygen to bubble through concentrated hydrochloric

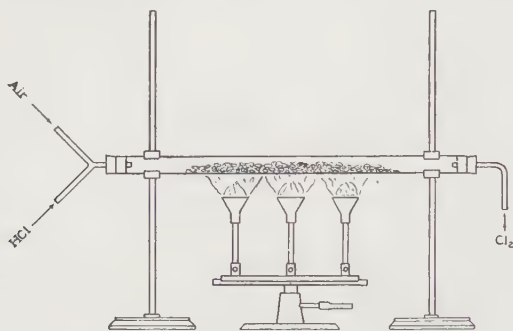


FIG. 100.

acid, HCl is carried into the tube, along with oxygen. The exit tube dips into a solution of potassium iodide and starch. Free chlorine displaces iodine, which colors starch blue. The Deacon process does not yield pure chlorine.

III. Methods Based Upon the Interaction of Oxidizing Agents and Hydrochloric Acid.

Concentrated hydrochloric acid interacts with almost any good oxidizing agent containing oxygen, chlorine being formed. In other words, HCl is oxidized by oxygen furnished by the oxidizing agent:

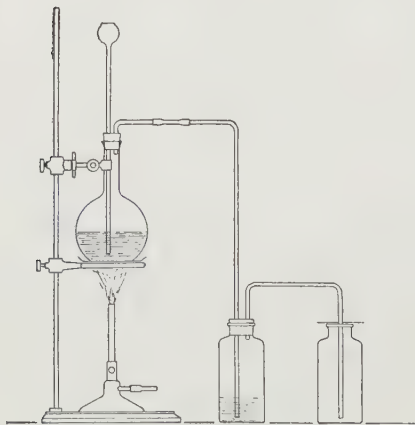


FIG. 101.

(1) *When manganese dioxide, MnO_2 , is treated in a flask with concentrated hydrochloric acid. On warming, chlorine is evolved. It may be freed from HCl by passing it through water contained in a wash-bottle, and then dried*

by passing the gas through a bottle containing some concentrated sulfuric acid. Since chlorine is much heavier than air, it may be collected by the upward displacement of the latter (Fig. 101).

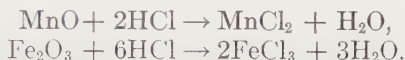
Mn in MnO_2 has a valence of 4. Unstable MnCl_4 is first formed, which decomposes into MnCl_2 and Cl_2 :



(Balance the above equation by the "electron" method.)

Other higher oxides similar to MnO_2 , as well as peroxides, yield chlorine when treated with concentrated hydrochloric acid.

Note that when lower oxides of metals are dissolved by hydrochloric acid, chlorine is not liberated:



The method just described is very commonly used in the laboratory for the preparation of chlorine. The mineral form of manganese dioxide (pyrolusite) is most convenient.

Chlorine also is frequently prepared by treating a mixture of MnO_2 and NaCl with sulfuric acid:



We may regard the action as first taking place between salt and H_2SO_4 :



HCl and MnO_2 may be regarded as interacting thus:



MnCl_2 would be decomposed by H_2SO_4 :



Equations (1), (2), and (3) represent the complete reaction as summed up above.

(2) *Chlorine is most conveniently prepared for use in the laboratory by the interaction of potassium permanganate and hydrochloric acid.* The permanganate is introduced into a flask and concentrated hydrochloric acid, diluted with one-third of its weight of water, is permitted to run in drop by drop from a dropping funnel, as shown in Fig. 102. The flask is gently warmed, if necessary, and the gas is evolved in a steady stream. By turning the stopcock, the generation of chlorine soon stops. The gas may be freed from HCl by bubbling it through a small quantity of water. The chemical change is as follows:

Skeleton:



Balanced:



Molecular:

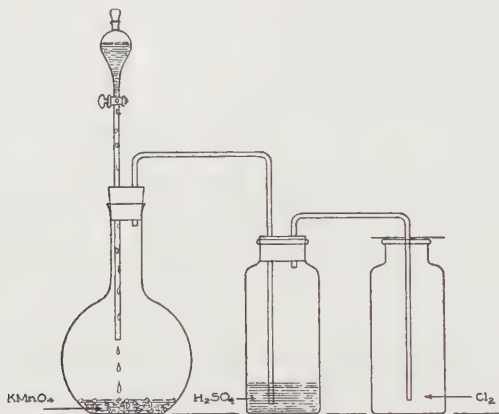
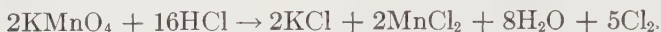


FIG. 102.

(Balance the above equation by the "ion-electron" method.) The permanganate method is an excellent one for preparing small quantities of chlorine, but is rather expensive.

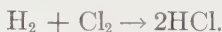
272. Physical Properties. — Chlorine is a greenish-yellow gas possessing a disagreeable smell. When breathed, it has an excessively irritating action upon the membranes of the nose and throat, producing coughing, inflammation, suffocation, and even death. The gas is about 2.5 times as heavy as air, one liter weighing 3.22 g., at S.T.P.

Chlorine may be readily condensed to a golden-yellow liquid, boiling at -33.6° . Its C.T. is 146° and its C.P. is 83.9 atmospheres. At 0° , only 6 atmospheres of pressure are required to liquefy it. Liquid chlorine may be frozen to a pale yellow solid which melts at -102° . Liquid chlorine is stored in strong lead-lined steel cylinders holding from 50 to 60 pounds. One volume of water at 20° dissolves about 2.15 volumes of chlorine.

273. Chemical Properties. — Chlorine is a very active substance (see Oxygen). It enters into direct combination with many substances, forming numerous compounds.

I. Chlorine and the Elements.

Chlorine enters into direct combination with most of the elements. Oxygen, nitrogen, carbon, argon, and the rare gases of the atmosphere are exceptions. A jet of chlorine may be burned in an atmosphere of hydrogen, and a jet of hydrogen will burn in an atmosphere of chlorine:



This may be shown by lowering a jet of burning hydrogen into a jar of chlorine (Fig. 103).

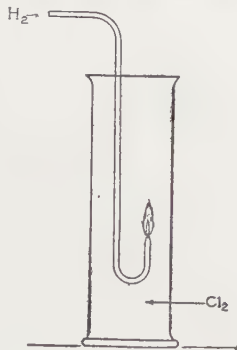
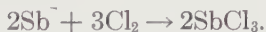


FIG. 103.

When a mixture of hydrogen and chlorine is kept in the dark, there is almost no union between the gases at ordinary temperatures; in diffused light, the union is very slow; but when exposed to the light of burning magnesium or to direct sunlight, the mixture explodes at once.

Chlorine combines readily with phosphorus to form PCl_3 or PCl_5 , the latter compound being formed when an excess of chlorine is used.

Chlorine combines readily with all the common metals except gold and platinum. Finely divided antimony, thin leaves of copper or of Dutch leaf (an alloy of Cu and Zn), and sodium burn in the gas, forming chlorides. Thus:



The combustion of antimony may be shown by sprinkling a little of the powdered metal into a jar of chlorine gas.

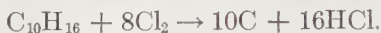
When chlorine and the metals are thoroughly dried, they do not combine; but when a trace of water is admitted, combination occurs, the water playing the rôle of a catalyst.

II. Chlorine and Compounds.

Chlorine is able to displace carbon, iodine, bromine, and sulfur from binary compounds. Thus, when a very dilute solution of KI is mixed with starch suspension and treated with a drop or two of chlorine water, iodine is liberated and colors the starch blue:



Also, if a tuft of cotton be dipped into hot turpentine and then thrust into a vessel containing chlorine, the turpentine ($C_{10}H_{16}$) is decomposed with the liberation of so much heat that combustion occurs:



The cloud of soot (carbon) formed shows that chlorine displaces carbon.

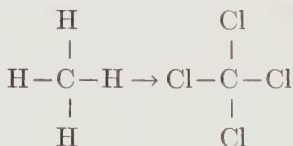
Chlorine may be substituted for other elements.

Thus, when methane or marsh gas (CH_4) is mixed with chlorine and the mixture exposed to sunlight, a slow action occurs:



One atom of chlorine is substituted for one of hydrogen to form a molecule of methyl chloride (CH_3Cl).

Note that in **substitution** a compound and an elementary substance interact to form two other compounds; no elementary substance is formed. (How does *substitution* differ from *displacement*?) By continuing the action of chlorine and light, the following substitution products may be obtained: CH_2Cl_2 , $CHCl_3$ (chloroform), and CCl_4 (carbon tetrachloride). The last compound is the final substitution product of methane:



Carbon tetrachloride is sometimes called tetrachlormethane.

When chlorine is dissolved in water, it interacts with the latter to form hydrochloric and hypochlorous acids:

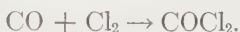


This action is *reversible*. When chlorine water is exposed to sunlight, $HClO$ loses oxygen. Hypochlorous acid is an active oxidizing agent, and is used extensively as a disinfectant and bleaching agent. Chlorine bleaches, therefore, in the presence of water; the bleaching action is really due to the fact that hypochlorous acid is formed, which decomposes, yielding oxygen. The decomposition of $HClO$ is accompanied by the liberation of much energy.

The bleaching action of chlorine may be shown by lowering moistened strips of highly colored cloth into jars of chlorine. A strip of dry cloth lowered into a cylinder of chlorine standing over concentrated sulfuric acid is not bleached, for the acid in the bottom of the cylinder absorbs the moisture.

Chlorine water bleaches ordinary writing ink (ferrous tannate), but not printer's ink (carbon).

Chlorine unites directly with certain compounds to form other compounds. Carbon monoxide and chlorine, when mixed and exposed to sunlight, combine to form **phosgene**, or **carbonyl chloride**, COCl_2 :



Phosgene is a colorless liquid, boiling at about 8° . It is a highly poisonous substance. Chlorine also unites with slaked lime, forming bleaching powder (307):



When a solution of chlorine water is cooled with ice, a greenish-yellow, crystalline *hydrate*, $\text{Cl}_2 \cdot 8\text{H}_2\text{O}$, is formed. The hydrate is unstable. Faraday (1823) obtained liquid chlorine by sealing chlorine hydrate in one limb of a strong bent glass tube, and placing that limb in warm water while the other limb was immersed in a freezing-mixture of salt and ice (Fig. 104).

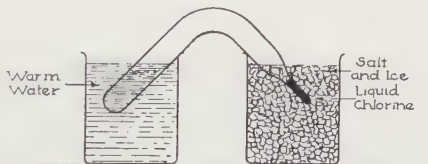


FIG. 104.

Northmore first liquefied chlorine under pressure in 1806. Faraday carried out more detailed investigations a few years later, and showed that many other gases could be liquefied. In these experiments, Faraday employed a bent glass tube as he did in the case of chlorine.

274. Uses of Chlorine. — Immense quantities of chlorine are used as a bleaching, disinfecting, and oxidizing agent. It is used on a large scale in the manufacture of bleaching powder or chloride of lime, which is the disinfectant commonly employed in the household. Chlorine also is used in liberating bromine from bromides and in the manufacture of chloroform (CHCl_3), carbon tetrachloride, and hypochlorites. Large quantities of chlorine were used in the World War.

Chlorine (or hypochlorous acid) is particularly effective as a germicide. It is used for bleaching cotton and linen goods and wood pulp, but is too active for silks and woolens.

275. **Chlorine in the World War.** — Great quantities of chlorine and of chlorine compounds were used in the World War. The first attack was made by the Germans on April 22, 1915. They previously stored the substance in steel cylinders containing 44 pounds each. These were concealed in the trenches, and the substance was employed in the form of gas clouds. As chlorine gas is about 2.5 times as heavy as air, the clouds were carried over the ground by the wind. Chlorine is a powerful respiratory irritant. In high concentration, it affects the eyes also. In a concentration of 1 part of chlorine to 10,000 parts of air, the struggle for breath becomes acute, and a man would probably be incapacitated in 5 minutes.

Some of the most important chlorine compounds used in gas warfare were *phosgene* (COCl_2), "*mustard gas*" ($(\text{C}_2\text{H}_4\text{Cl})_2\text{S}$), and *chloropicrin*, or *nitrochloroform* (CCl_3NO_2). Phosgene is chiefly a respiratory irritant, but is more poisonous than chlorine. "Mustard gas" produces serious burns, and in severe cases the larynx, bronchial tubes, and lungs are attacked. Chloropicrin induces coughing, nausea, vomiting, and unconsciousness. Some of the secondary effects are asthma, weak heart, and gastritis.

In 1917–1918 the United States built a chlorine plant at Edgewood, Md., having a capacity of 100 tons daily. This was the largest chlorine plant ever constructed.

BROMINE. $\text{Br} = 79.92$

276. **History and Occurrence.** — Bromine was discovered by the French chemist Balard in the year 1826; he named the element **bromine** (Greek, *a stench*).

Bromine usually occurs as bromides, particularly as MgBr_2 and NaBr . These salts are found in certain mineral springs, those in Ohio containing from 3.4 to 3.9 per cent of MgBr_2 . It also is found in the upper layers of beds of rock salt. The potash beds of Stassfurt and the salt brines of Michigan, Ohio, and West Virginia are the commercial sources of bromine. The mother-liquor of the salt industry ("bittern") contains MgBr_2 and a smaller quantity of NaBr . Sea-water contains on an average about 0.0064 per cent of bromine, which means that about one pound of bromine could be obtained from 1,800 gallons of sea-water.

Before the beginning of the present century, Germany produced most of the bromine; but for a good many years the average annual production in the United States has been about 1,000,000 pounds. In 1924, over 2,000,000 pounds were produced, the

largest portion coming from the brines of the Saginaw Valley, Michigan.

277. Preparation. — Some of the methods employed in the preparation of bromine are similar to those for preparing chlorine: a bromide is used instead of a chloride.

I. The Electrolysis of Bromides.

At Midland, Michigan, the brine pumped up from the underlying salt-beds is concentrated to crystallize out common salt, and the remaining liquor, known as *bittern*, is subjected to electrolysis, bromine being set free at the anode. Bromine is less active than chlorine, so it is largely liberated by the current before chlorine is set free.

II. By the Interaction of HBr and an Oxidizing Agent.

This method is generally employed in the laboratory, and also is the basis of one of the manufacturing methods for bromine. In the laboratory, a bromide, manganese dioxide, and dilute sulfuric acid are mixed in a retort, the bromine distilled off, and collected in a test-tube surrounded by cold water. In case sodium bromide is used, the equation for the reaction is:



In the Ohio River Valley, bittern is mixed with H_2SO_4 and NaBrO_3 (sodium bromate):



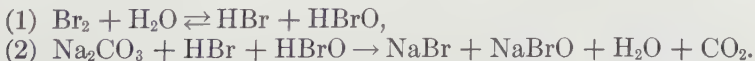
III. By Treating a Bromide with Chlorine.

Bromine is produced industrially by treating a solution of a bromide with a current of chlorine gas:



Chlorine is more active than bromine and iodine and therefore displaces them from halides.

In the preparation of bromine, the vapor may be cooled and condensed as a liquid; but much of the vapor is absorbed by leading it through a splash tower against a "counter current" of a solution of sodium carbonate. The chemical changes are shown by the following equations:



The solution containing NaBr and NaBrO is evaporated to dryness, NaBrO changing into NaBrO₃ and NaBr:



Bromine is liberated by adding sulfuric acid. Since it is easier and safer to ship the dry salt mixture to a distant consumer than to ship the liquid, this is often done, and the consumer adds sulfuric acid as the bromine is needed.

To insure against a shortage of bromine, the Ethyl Gasoline Corporation in coöperation with the duPont Company has conducted experiments for the recovery of bromine from the bromides of sea-water. A vessel was equipped capable of recovering 100,000 pounds of the element per month. It has been reported that the trial trip of this "bromine ship" was quite successful; indeed, the production was beyond the rated capacity.

278. Physical Properties. — Bromine is a dark-red liquid which boils at 59°. Bromine and mercury are the only liquid elements at ordinary temperature. The specific gravity of bromine is about 3.18. About 4 parts of bromine are soluble in 100 parts of water. The vapor of bromine possesses a dark-red color and a very disagreeable odor; it attacks the eyes very painfully and produces great irritation when inhaled. When taken internally it acts as an irritant poison, and when brought in contact with the skin it produces sores which are difficult to heal.

279. Chemical Properties. — In its chemical deportment bromine resembles chlorine, but is less active. Thus, it combines directly with certain metals and non-metals, though its action is not as energetic as that of chlorine. Bromine also acts as a bleaching and oxidizing agent, but less quickly than does chlorine. At 228°, the density of bromine vapor is 5.525 (air = 1), showing that the molecule is diatomic, Br₂. At 1,050°, however, it begins to dissociate into monatomic molecules:



280. Uses. — Bromine is used in the manufacture of some of the coal-tar dyes; for preparing KBr and NaBr; and in analytical and synthetic chemistry. KBr and NaBr are used in medicine as sedatives and in preparing AgBr, which is employed extensively in photography as the sensitive material on the plate. A considerable quantity of bromine was used during the World War in the manufacture of **lachrymators** ("tear gases"): *e.g.*, bromo-acetone.

“Solidified bromine” is convenient for laboratory work. Sticks of the siliceous earth known as “kieselguhr” are pressed with size or molasses, burned until coherent, and then soaked in bromine. The porous material absorbs as much as 75 per cent of its own weight of the liquid.

There has been in recent years an increased demand for bromine because of the fact that it is added in the form of ethylene bromide ($\text{C}_2\text{H}_4\text{Br}_2$) to “leaded” gasoline, *i.e.*, to gasoline containing tetraethyl lead, $\text{Pb}(\text{C}_2\text{H}_5)_4$. About two cubic centimeters of ethylene bromide are added to each gallon of leaded gasoline (ethyl gasoline). The ethylene bromide is used to furnish bromine for transforming the lead of the tetraethyl lead into lead bromide; otherwise the free lead would injure the ignition-points.

IODINE. $I = 126.93$

281. History and Occurrence. — Iodine was discovered in 1812 by Courtois, a manufacturer of saltpeter, near Paris, who obtained it from the mother-liquor of salts produced from burnt seaweed, or *kelp*. The liquid was heated with sulfuric acid in a retort, “a vapor of a superb violet color” being obtained, which condensed in the form of brilliant crystals. The element was subsequently examined by Davy, and much more in detail by Gay-Lussac, who established its elementary nature and first proposed the name **iodine** (Greek, *violet*) on account of the color of its vapor.

Iodine occurs in combination in small quantities, but widely distributed, both in the organic and inorganic kingdoms. It occurs in sea-water, in sea-plants and sea-animals, and in the thyroid gland of man and of animals. Formerly, the only commercial source of iodine was seaweed, which was collected along the rocky coasts of Scotland, Ireland, and France. Certain sea-plants, in growing, extract iodine from water. Thus, the giant sea-plants, known as *kelp*, which grow along the Pacific coast, not only contain potassium chloride but a small quantity of iodides. For some years most of the iodine of commerce has been obtained from sodium iodate (NaIO_3), which is found in small quantity in Chile saltpeter, or crude sodium nitrate.

282. Preparation. — In general, the methods used in the preparation of iodine are similar to those used for bromine (see Chlorine also).

I. Laboratory Method. Iodine is usually prepared in the laboratory by treating a mixture of an iodide and manganese

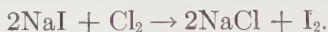
dioxide with fairly concentrated sulfuric acid:



The mixture of solids and sulfuric acid may be gently heated in a retort and the iodine vapor condensed very much as bromine is prepared; or, the mixture may be carefully heated in a beaker and the iodine condensed upon the bottom of a small flask containing cold water.

This laboratory method is the basis of a commercial method employed in extracting iodine from the ash of seaweed.

II. By Treating an Iodide with Chlorine:



As chlorine is much more active than iodine, it readily displaces the latter element. The iodine is driven off as vapor and then condensed.

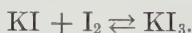
III. From the Mother-Liquors of Chile Saltpeter (Chief Commercial Method). The mother-liquor remaining after crystallizing NaNO_3 from a solution of Chile saltpeter is treated with sodium bisulfite and sodium sulfite:



The precipitated iodine is washed on filters made of coarse canvas or bagging, and then subjected to pressure to remove water. The iodine is purified by sublimation.

Sublimation is the distillation of a solid when a condensation of the vapor takes place directly to the solid state.

283. Physical Properties. — Iodine is a shining, blackish-gray solid, which crystallizes in the rhombic system. It is the heaviest of the halogens, having a specific gravity of 4.948 at 17° (Stas). Iodine melts at about 114° and boils at 184° , giving a violet vapor which turns blue on strongly heating. Iodine is sparingly soluble in water. The best solvents for iodine are alcohol, carbon disulfide, chloroform, and an aqueous solution of potassium iodide (or other iodides). An alcoholic solution of iodine is brown in color, probably due to feeble union with the solvent. Carbon disulfide and chloroform solutions of iodine are violet. Iodine is very soluble in a solution of an iodide, owing to chemical action between the iodide and iodine:

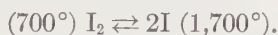


"Tincture of iodine" consists of iodine, potassium iodide, and alcohol.

A trace of iodine colors starch "solution" a deep-blue. This is a most delicate test for the element.

284. Chemical Properties. — In its chemical properties, iodine resembles chlorine and bromine, but is less active, being displaced from iodides by the former. It unites directly with many of the metals and non-metals, accompanied by heat and light: *e.g.*, white phosphorus soon bursts into flame when brought in contact with iodine. Chlorine and bromine combine with hydrogen much more readily than does iodine. The element, like chlorine and bromine, interacts with solutions of soda and potash (306). Iodine is an oxidizing agent.

The specific gravity of iodine vapor up to 700° is 8.72 (air = 1), which shows that the molecular weight is 253.84, and the molecule therefore diatomic. Above 700° its density begins to diminish, and at $1,700^{\circ}$ it becomes constant and is just half that of the vapor below 700° . This proves that the diatomic molecule dissociates (197):

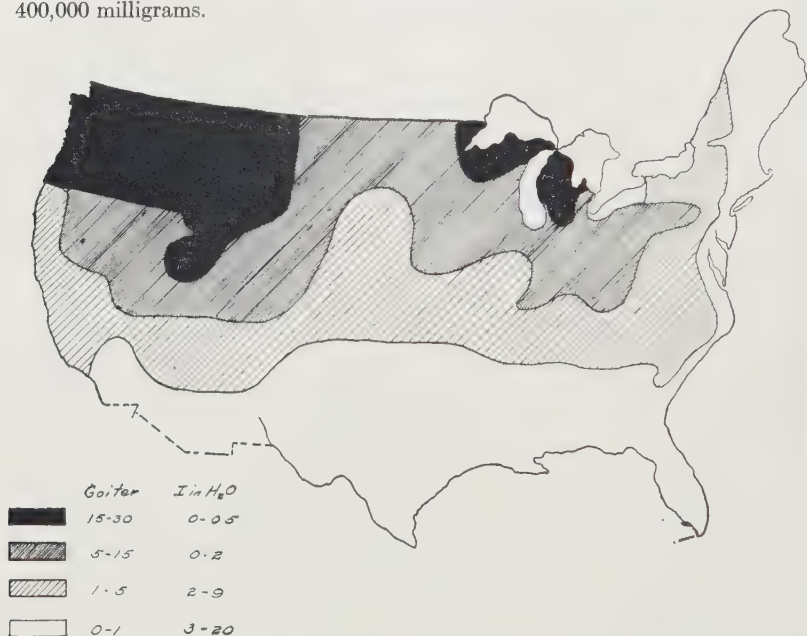


285. Uses of Iodine. — Iodine is used in the manufacture of certain coal-tar dyes, organic compounds, iodoform (CHI_3), KI, and NaI; in medicine, photography, and in chemical analysis. "Tincture of iodine" is effective in reducing certain swellings and as a germicide.

Iodine is an essential constituent of the animal body. It is estimated that there are approximately 20 milligrams in the body of a normal adult, about one-half of which is in the thyroid gland near the Adam's apple. It is very important to keep the iodine content of the body well regulated. A subnormal secretion of iodine may give rise to simple or fibrous *goiter* or to *cretinism*, which is accompanied by lowered muscular activity and dullness of mind. There is apparently a close connection between the prevalence of goiter and cretinism and the deficiency of iodides in drinking-water and foodstuffs. Goiter and cretinism are prevalent in the central Alps and in the regions of the Great Lakes and of the Rocky Mountains, due, it is believed, to the insufficiency of iodides (Fig. 105).

Some years ago Dr. E. C. Kendall, of the University of Minnesota, isolated and identified the active principle of the thyroid gland, which is called **thyroxine**; it is a complex organic compound, the constituents of which are carbon, hydrogen, oxygen, nitrogen, and iodine. As the result of much patient and careful research, its constitution is known, and Dr. C. R. Harrington of London has synthesized thyroxine. It is beneficial in the treatment of such

diseases as goiter and cretinism. Thyroxine appears to be a powerful catalyst. When an injection of only 1 milligram is made, the increase in the output of carbon dioxide from the body is enormously increased, amounting to about 400,000 milligrams.



Courtesy, J. W. Turrentine, United States Department of Agriculture.

FIG. 105. Goiter Map of the United States.

Distribution of goiter and comparison of iodine water-supplies: goiter rate per thousand population; iodine in parts per billion of representative rivers.

There is another form of goiter, known as *exophthalmic goiter*, which is the result of an excessive absorption of iodine. The symptoms of this affliction are an enlarged thyroid gland, accompanied by protruding eyeballs, palpitation of the heart, and anemia.

A small quantity of sodium iodide is sometimes added to table salt in order to supply the body with sufficient iodine to prevent goiter. J. W. Turrentine, of the United States Department of Agriculture, has suggested the use of dried kelp, which contains an appreciable amount of iodine compounds. Iodine is supplied by certain foods, such as spinach, lettuce, string beans, butter, and milk.

FLUORINE. $F = 19.0$

286. History and Occurrence. — The brilliant French chemist Moissan (1886) achieved the difficult task of preparing fluorine. Long before Moissan succeeded in liberating fluorine, it was known

that fluorspar contained calcium in combination with an element analogous to chlorine. The element was named "fluorine," owing to the use of fluorspar as a flux (Lat. *fluo*, I flow) in metallurgy.

Fluorspar, CaF_2 , is the most common mineral containing fluorine. Fluorine occurs in large quantities in the mineral **cryolite**, $3\text{NaF} \cdot \text{AlF}_3$, which is found in Greenland. Fluorine also occurs in a large number of other minerals, and in very small quantities in certain mineral waters and in sea-water. It also is found in bones of animals and in the teeth, and traces have been detected in the blood, milk, and brains of animals.

287. Preparation. — Fluorine was first prepared by Moissan, who passed an electric current through pure, anhydrous hydrogen fluoride containing potassium hydrogen fluoride (KHF_2) in solution to make it a conductor. The electrolysis was carried out in a U-tube constructed of platinum or of an alloy of platinum and iridium. The electrodes were made of platinum and iridium, and the tube was fitted with stoppers of fluorspar, as shown in Fig. 106. The tube containing the solution was surrounded by methyl chloride, which boiled and kept the temperature at about -23° . It was learned subsequently that copper vessels may be employed instead of those constructed of the more expensive metals; also, artificial graphite. Hydrogen is evolved at the cathode and fluorine at the anode, where they pass off by side-tubes.

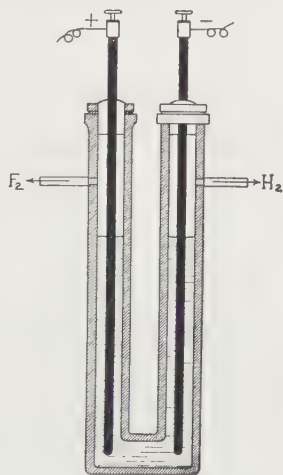


FIG. 106.

Molten potassium hydrogen fluoride (KHF_2) and the analogous sodium compound readily yield fluorine when subjected to electrolysis.

288. Properties of Fluorine. — Fluorine is a pale greenish-yellow gas about 1.3 times as heavy as air. It may be condensed to a pale yellow liquid, which boils at -187° .

In its chemical action fluorine is very similar to chlorine, but much more active. In fact, fluorine is the most active element known. Thus, it combines explosively with hydrogen in the dark; and many elements, such as sulfur, phosphorus, carbon, silicon, and boron, catch fire in fluorine. Most metals also burn in fluo-

rine, but gold and platinum are but slightly attacked below a red heat. Fluorine displaces chlorine, bromine, and iodine from their halides; also, oxygen from water, converting it into ozone:



It is an interesting fact that fluorine does not combine with oxygen or nitrogen. Fluorine still possesses very great chemical activity at the lowest temperatures attainable.

THE HALOGEN ACIDS

289. **Introductory.** — We have seen (266) that the halogens combine directly with hydrogen to form similar compounds:



These are colorless gases (hydrogen fluoride boils at 19°), very soluble in water, forming important acids. In general, the halides of hydrogen may be liberated by treating their salts with acids. Since the stability of the hydrogen compound decreases with increase of the atomic weight of the halogen, HBr and HI are effective reducing agents and therefore yield more or less bromine and iodine when a bromide or an iodide is treated with strong sulfuric acid.

Aqueous solutions of HCl, HBr, and HI are strong acids, but hydrofluoric acid is relatively weak.

HYDROGEN CHLORIDE

(Hydrochloric acid. Muriatic acid)

290. **History.** — Hydrochloric acid, a solution of hydrogen chloride in water, was obtained by Glauber, about 1648, by the interaction of common salt and sulfuric acid. Priestley (1772) was probably the first experimenter to collect gaseous hydrogen chloride. He collected the gas over mercury, and named it *marine-acid air*, because it was produced by the decomposition of sea-salt.

291. **Occurrence.** — Hydrochloric acid gas occurs in the gaseous exhalations of certain active volcanoes, especially in Vesuvius. Hydrochloric acid is found in the waters of several of the South American rivers which rise in the volcanic districts of the Andes. It is an important component of the gastric juice of man and of

animals; the gastric juice of man contains from 0.2 to 0.4 per cent, while that of dogs contains 0.6 per cent.

292. Preparation.—I. **Formation of Gaseous Hydrogen Chloride.**

(1) *By direct union of hydrogen and chlorine.*

When equal volumes of hydrogen and chlorine are mixed and exposed to the light of burning magnesium or to sunlight, the gases combine with explosive violence:



This reaction is another illustration of Gay-Lussac's law of volumes (152).

(2) *By the interaction of chlorine and hydrogen compounds.*

Chlorine has such great affinity for hydrogen that it withdraws this element from all its compounds except hydrogen fluoride. Thus, it decomposes such compounds as ammonia (NH_3), hydrogen sulfide (H_2S), hydrocarbons ($\text{C}_{10}\text{H}_{16}$, etc.).

II. Laboratory Preparation of Hydrogen Chloride.

Common salt is warmed in a flask with sulfuric acid previously diluted by pouring the acid into about one-third of its weight of water (Fig. 107). As the gas is heavier than air, it may be collected by the upward displacement of the latter. When an excess of acid is used and the action carried out by the gentle application of heat, the chemical change is as follows:

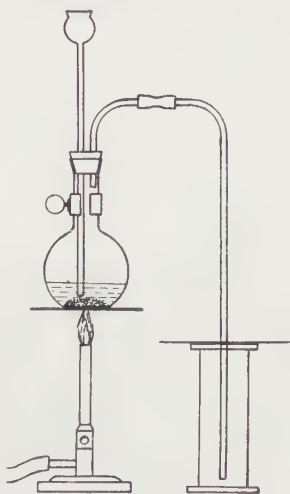


FIG. 107.

NaHSO_4 is a white solid; it is an acid salt, for the molecule contains hydrogen replaceable by a metal. The salt is often called *acid sodium sulfate*, or *sodium hydrogen sulfate*.

It should be noted that other chlorides, such as KCl and NH_4Cl , can be substituted for NaCl , but the last substance is the cheapest source of both chlorine and hydrochloric acid gas.

Other stable acids with high boiling points might be used instead of H_2SO_4 , but in practice none is as serviceable as sulfuric acid; for it is cheap, relatively stable, and possesses a high boiling point (338°).

HCl may be dried by passing it through concentrated sulfuric acid.

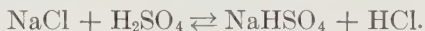
Note that the above action is *reversible*. If a concentrated solution of NaHSO_4 is treated with concentrated hydrochloric acid, NaCl is precipitated.

When solid salt is treated with concentrated sulfuric acid the action is driven to the right, especially when HCl is expelled by heat; but when water is present and the temperature of the solution kept relatively low, the action comes to equilibrium before completing itself. (Explain this fully in terms of molecules.)

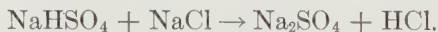
III. Commercial Preparation of Hydrochloric Acid.

Hydrochloric or muriatic acid is manufactured on a very large scale by dissolving hydrogen chloride in water. HCl is a by-product of the Leblanc soda process, and in the early days of the soda industry the gas was allowed to escape into the air. As it killed the vegetation, manufacturers were required to absorb it in water.

The first action that takes place when the acid and salt are heated is as follows:



At a higher temperature the action completes itself:



The commercial acid is usually of a yellow color, due to impurities, chiefly ferric chloride.

293. Physical Properties of Hydrogen Chloride. — Hydrogen chloride is a colorless gas possessing a sharp odor. It can be condensed to a colorless liquid, the C.T. being 51.4° and the C.P. 81.55° atmospheres. It solidifies to a white crystalline mass, melting at -111.4° . The gas is about 1.25 times as heavy as air. HCl is extremely soluble in water. At 0° , 506 volumes dissolve in 1 volume of water, and at 20° , 442 volumes. The solubility of the gas may be strikingly shown by the following *experiment*:

A large heavy round-bottomed flask is filled nearly full of water to which a small quantity of blue litmus solution is added. The flask is then fitted

with a rubber stopper and two glass tubes, as shown in Fig. 108. A similar flask is filled with carefully dried HCl, fitted with a rubber stopper and a glass tube which extends well up into the flask. This flask is then inverted over the other flask, and the two straight tubes are connected by means of rubber tubing. By blowing into the end of the bent tube, a drop of water is forced into the upper flask, and as it dissolves hydrogen chloride at once, a partial vacuum is produced and more water is driven into the upper flask, producing a fountain. Since hydrochloric acid is formed, the litmus solution turns red.

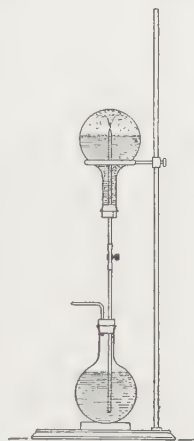


FIG. 108.

Concentrated hydrochloric acid usually contains between 35 and 40 per cent of hydrogen chloride. An acid containing about 39 per cent of HCl has a specific gravity of 1.2. Water saturated with the gas at 15° contains about 43 per cent of HCl, its specific gravity being about 1.22. On heating a saturated solution of the gas, the liquid loses HCl faster than it does water, and the residual liquid becomes weaker until it finally contains 20.24 per cent of HCl. The solution then boils unchanged at 110°, under normal atmospheric pressure. When dilute hydrochloric acid is boiled, it loses water faster than it does HCl. Finally, when the concentration of acid reaches 20.24 per cent, it boils constantly at 110°, yielding a product of constant composition.

294. **Chemical Properties.** — HCl is a very stable compound. At 1,800°, the gas begins to dissociate into its elements.

Hydrogen chloride and ammonia gas (NH₃) unite with the greatest readiness to form a white cloud of ammonium chloride (NH₄Cl):

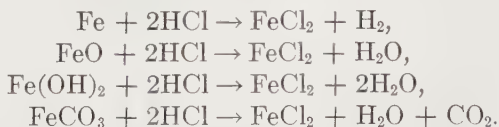


HCl does not interact with the non-metals, but the more active metals displace hydrogen when brought in contact with it.

The aqueous solution of HCl (hydrochloric acid) is one of the most active and important acids. Its deportment is entirely different from that of gaseous, liquid, or solid hydrogen chloride. Hydrochloric acid is a good conductor of electricity and reddens blue litmus, while hydrogen chloride is practically a non-conductor and does not possess the characteristics of acids.

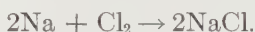
Hydrochloric acid is a powerful solvent, and it forms with many metals and compounds of metals an important class of salts

known as **chlorides**. Its interaction with iron and certain iron compounds may be regarded as typical:

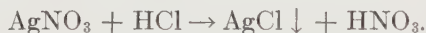


In general, we may state (1) that metals preceding hydrogen in the order of activity (126) displace hydrogen from hydrochloric acid; (2) that oxides and hydroxides of metals interact with hydrochloric acid to form chlorides and water; and (3) that carbonates interact with hydrochloric acid to form chlorides, water, and carbon dioxide.

Chlorides also may be prepared by other methods. Thus, a chloride may be prepared by synthesis:



Again, a chloride may be obtained by double decomposition:



As AgCl is extremely insoluble, a solution of AgNO_3 is used as a test for chlorides.

The only common chlorides extremely insoluble in water are AgCl and Hg_2Cl_2 (mercurous chloride). PbCl_2 is sparingly soluble in cold water, but fairly soluble in very hot water.

295. **Composition of Hydrogen Chloride.** — (1) When hydrochloric acid is subjected to electrolysis, one volume of hydrogen to one of chlorine is obtained. The *Brownlee apparatus* is very convenient for demonstrating this fact (Fig. 109). Electrodes of carbon are employed.

(2) Chlorine and hydrogen are generated in a dimly lighted room by the electrolysis of hydrochloric acid, and the mixture of the two gases is passed through concentrated sulfuric acid to remove the moisture; then through a long glass tube provided with two stopcocks, until all the air is displaced (Fig. 110). By closing the stopcocks, the mixture of the two gases is at atmospheric pressure. If one of the stopcocks is now opened and the end of the tube forced down into a tall cylinder containing a solution of potassium iodide, chlorine displaces iodine, which dissolves, leaving hydrogen.

The volume of residual gas is one-half that of the mixture, *i.e.*, it is equal to that of the chlorine.



(3) When HCl is confined over mercury and then decomposed by the introduction of sodium, the residual hydrogen occupies one-half of the volume of the hydrogen chloride:

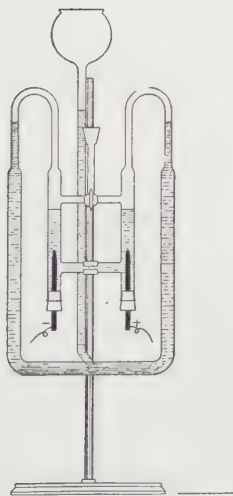
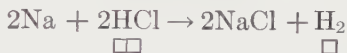


FIG. 109.

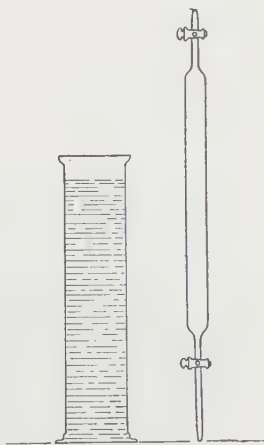
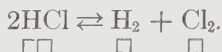


FIG. 110.

These experiments show that two volumes of HCl yield one volume of hydrogen and one of chlorine:



296. **Uses of Hydrochloric Acid.** — Hydrochloric acid is used as a solvent; for the preparation of chlorides and chlorine; as a laboratory reagent; in dyeing and calico printing; to clean the surfaces of metals; it also is used in medicine, and plays an important rôle in digestion.

HYDROGEN BROMIDE

(Hydrobromic Acid)

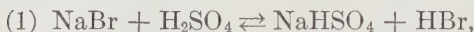
297. **Preparation and Properties.** — Hydrogen bromide, HBr, is best prepared by treating phosphorus tribromide with water:



HBr may be readily trapped in water, forming hydrobromic acid; or it may be collected by upward displacement of air.

Instead of starting with PBr_3 , it is the practice to mix red phosphorus with about three times its weight of sand, introduce the mixture into a flask, and then wet it with a small quantity of water. Bromine is run in slowly from a dropping-funnel. Phosphorus and bromine first unite to form PBr_3 , which is decomposed by the water. The U-tube contains red phosphorus and glass beads to absorb any bromine that may escape from the flask.

Hydrogen bromide cannot be successfully prepared by treating a bromide with strong sulfuric acid (see HCl, 292), owing to the fact that HBr is less stable than HCl; therefore it tends to reduce sulfuric acid to sulfurous acid, which dissociates, yielding sulfur dioxide. At the same time, HBr is oxidized (loses hydrogen) to free bromine. The chemical equations showing the interaction of a bromide and concentrated sulfuric acid may be written thus:

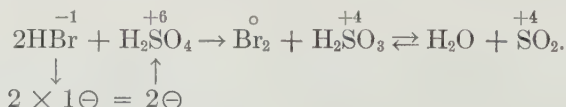


(Review Oxidation and Reduction, Chap. XV.)

The equation showing the action of H_2SO_4 upon HBr, may be balanced by the "electron" method:



Since two electrons are required to reduce the valence of sulfur from +6 to +4, we need two molecules of HBr:



H. N. McCoy has worked out a method for preparing a solution of HBr, which is based upon heating a mixture of a saturated solu-

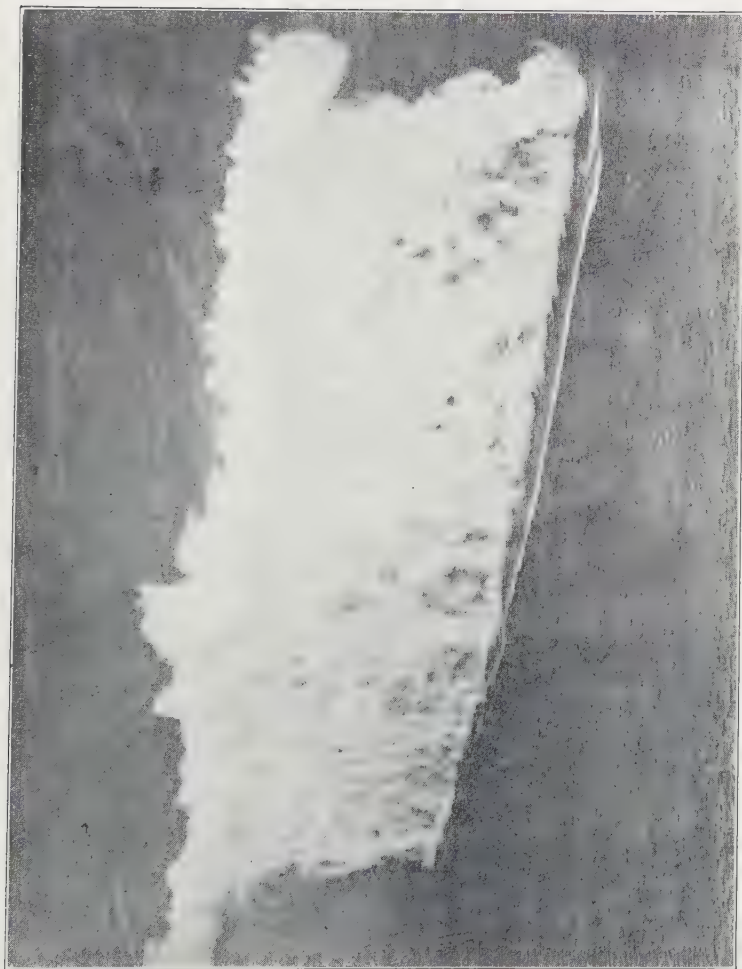


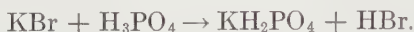
FIG. 111. Smoke Curtain.

Courtesy of the Chemical Warfare Service.

The curtain shown here was emitted in the demonstration of the sinking of the Battleship West Virginia, Cape Hatteras, N. C., Sept. 5, 1923.

tion of KBr and slightly diluted sulfuric acid. The distillate is hydrobromic acid of constant boiling point.

Pure hydrogen bromide may be obtained by heating a bromide with phosphoric acid:

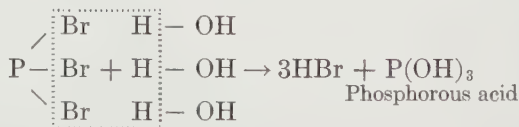


Hydrogen bromide is very similar to hydrogen chloride, but is not so stable. It is a colorless gas with a sharp odor and is extremely soluble in water. Its aqueous solution is called hydrobromic acid, which is very active, *i.e.*, it furnishes a high concentration of hydrogen-ion:



The salts of hydrobromic acid are known as **bromides**. They are analogous to chlorides. Chlorine displaces bromine from bromides.

298. **Hydrolysis.** — Many substances in the presence of water undergo double decomposition or **hydrolysis** (Greek, *water + to loosen*). Thus, the halides of phosphorus and of other non-metals are decomposed by water:

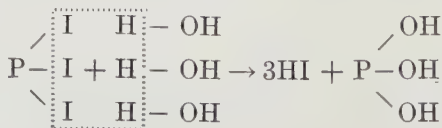


Hydrolysis plays an important part in the production of smoke screens or curtains. Titanium chloride (TiCl_4), for instance, may be carried by an airplane, and when the liquid is sprayed into the air it interacts with water vapor, producing a screen. (Write the equation.) A smoke curtain is shown in Fig. 111.

HYDROGEN IODIDE

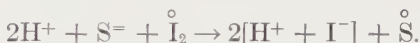
(Hydriodic Acid)

299. **Preparation.** — Hydrogen iodide, like hydrogen bromide, *can best be prepared by hydrolysis*:



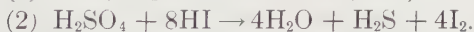
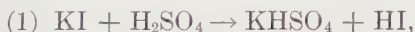
The apparatus is similar to that used in preparing HBr. A mixture of red phosphorus and iodine is introduced into the flask and water is allowed to flow in very slowly from the dropping-funnel [Care!]. The gas may be collected by the upward displacement of air, or it may be allowed to pass over into bottles containing water, in which it dissolves freely. The U-tube containing moistened red phosphorus absorbs any iodine which may escape from the flask.

An aqueous solution of HI may be prepared by allowing hydrogen sulfide to pass into water containing finely divided iodine in suspension. Iodine displaces the sulfide-ion:



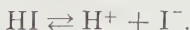
The precipitated sulfur may be removed by filtration, or the sulfur may be allowed to settle and the solution drawn or poured off.

HI, being even more unstable than HCl and HBr, cannot be prepared by treating an iodide with sulfuric acid. Sulfuric acid may be reduced to hydrogen sulfide:



HI is oxidized to free iodine, for it loses hydrogen.

300. Properties: Hydriodic Acid. — Hydrogen iodide is similar to HCl and HBr. It is a colorless gas with a sharp odor and is extremely soluble in water, forming hydriodic acid, which is highly ionized:



HI is much less stable than the other halogen acids, and for this reason is a good reducing agent. Aqueous solutions of HI do not keep well.

Hydrogen iodide is readily decomposed by heat. At 448°, about 21 per cent of its molecules are dissociated (215):



The salts of hydriodic acid are called **iodides**. KI and NaI are extremely soluble in water, but PbI_2 (yellow), AgI , Hg_2I_2 , and HgI_2 (scarlet) are practically insoluble.

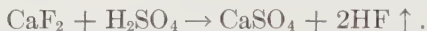
HYDROGEN FLUORIDE

(Hydrofluoric Acid)

301. **Preparation.** — Hydrogen fluoride is best prepared by heating potassium hydrogen fluoride:



The gas may be readily condensed to a liquid. For preparing a solution of hydrogen fluoride, fluorspar is treated with concentrated sulfuric acid in a platinum or lead vessel, heat being applied:



The vapor may be condensed to a liquid or absorbed in water, the solution being known as hydrofluoric acid. The acid may be preserved in bottles made of ceresin or of gutta-percha.

302. **Properties of Hydrogen Fluoride.** — Hydrogen fluoride is a colorless liquid, boiling at 19.4° and solidifying at -102.5° . It is very soluble in water. Pure hydrogen fluoride is a non-conductor of electricity.

The vapor density of hydrogen fluoride varies rapidly with change of temperature and pressure. This means that its molecular weight is not constant. At about 33° its vapor density corresponds to a molecular weight of approximately 38, indicating that the formula is H_2F_2 at that temperature; but at 90° the molecular weight is about 20 (HF), while at 26° the molecular weight of the vapor is 51, indicating that it is mainly a mixture of H_2F_2 and H_3F_3 . At the lower temperatures, association of two or more molecules of HF appears to occur:

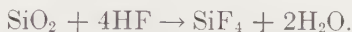


Potassium hydrogen fluoride (KHF_2) is regarded as an acid salt of H_2F_2 .

It should be noted that hydrogen fluoride is poisonous. Hydrofluoric acid also produces wounds, which heal with difficulty! Great care must be exercised, therefore, in handling this acid. Professor Nicklès of Nancy died, in 1869, from accidentally breathing the vapor of the acid while trying to prepare fluorine.

Hydrofluoric acid is rather a weak acid. Its most characteristic chemical property is its action upon silica and glass (*etching*).

Silica (SiO_2) is converted into silicon tetrafluoride, SiF_4 , a gaseous substance:



Pure silica may be completely volatilized by heating it in a platinum vessel with hydrofluoric acid. Ordinary glass may be regarded as being composed principally of silicates of sodium and calcium, and when exposed to hydrofluoric acid, fluorides and water are formed:



In etching, the surface of the glass is first covered with paraffin or beeswax, and with a sharp instrument some of the wax is removed in order to expose the glass to the acid. The etching may be accomplished either with the vapor or the aqueous solution. The vapor gives a rough surface where the glass is exposed, and the aqueous solution makes smooth depressions.

Henry Schwanhardt of Nürnberg invented the engraving of glass with hydrofluoric acid; he used it in the seventeenth century.

EXERCISES

1. Outline the relationships and general characteristics of the elements of the Halogen Family. How are they related to manganese?

2. Discuss the occurrence and the relative abundance of the halogens.

3. Give the comparative methods for preparing the halogens.

4. Explain thoroughly how chlorine is produced by electrolysis of brine. What other important products are obtained?

5. Discuss from the standpoint of chemical equilibrium the Deacon process for chlorine.

6. Write chemical equations to show the preparation of chlorine by starting with each of the following substances: (1) barium peroxide; (2) sodium chlorate; (3) lead dioxide; (4) potassium permanganate; and (5) potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$).

7. State the chemical properties of chlorine and write equations to show its action upon (1) water; (2) methane; (3) turpentine; (4) lime; (5) carbon monoxide.

8. Explain as fully as you can why chlorine is an efficient bleaching and oxidizing agent. What sort of materials are bleached by the use of chlorine? Why cannot it be used for bleaching silks, woolens, etc.? (See Hydrogen Peroxide.)

9. How did Faraday effect the liquefaction of chlorine and other gases?

10. How many cc. of $N/10$ chlorine water must be added to a solution containing 1 g. of magnesium bromide in order to liberate all the bromine?

11. Explain fully, also illustrate, the difference between displacement and substitution. Would you regard either one of these as being oxidation?

12. Chlorine is a good oxidizing agent. Explain fully the meaning of this statement.

13. Outline two different methods for obtaining pure silver from AgCl .

14. Explain how bromine and iodine are obtained industrially, and compare their chemical properties with those of chlorine.

15. Show how chlorine may displace bromide-ion, and how iodine may displace sulfide-ion.

16. Give names and formulae of the two most important minerals containing fluorine. By whom and how was the element first isolated? What other method may be used for preparing fluorine? What are the physical and the chemical properties of fluorine?

17. Outline the preparation and the properties of the hydrides of the halogens, as well as their aqueous solutions.

18. Account for the fact that HF and HCl are more stable than HBr and HI . Discuss from the standpoint of chemical equilibrium the synthesis of hydrogen iodide from its elements.

19. Using the "ion-electron" method, write equations to show why HI cannot be prepared by treating an iodide with H_2SO_4 .

20. Define, and also illustrate, hydrolysis.

21. Arrange the halogens, together with sulfur and oxygen, in the order of their activity. Why does a solution of HI darken on exposure to oxygen?

22. How is glass etched? Write equations to show the chemical changes.

23. Show how the volume relations of hydrogen chloride, hydrogen, and chlorine may be demonstrated.

24. (a) How much sodium chloride would be required to prepare 100 g. of hydrochloric acid containing 12.5 per cent of hydrogen chloride?

(b) How many grams of marble containing 99.5 per cent of calcium carbonate could be dissolved in the acid, and what weight and what volume of CO_2 would be liberated, assuming that the temperature is 20° and the pressure 750 mm.?

25. 4.305 g. of pure silver chloride were introduced into a porcelain boat, the boat and its contents placed inside a hard glass tube, and then heated to a high temperature, while pure, dry hydrogen was passed over it until nothing but pure silver was left in the boat. The hydrogen chloride formed was absorbed in soda-lime, the weight of which was increased by 1.0950 g. The weight of silver was found to be 3.240 g. Given the atomic weight of silver as 107.88 and hydrogen as 1.008, find the equivalent weight of chlorine and the ratio by weight of hydrogen and chlorine in hydrogen chloride.

26. Explain why an aqueous solution containing 20.24 per cent of HCl boils constantly at 110°C. , under standard atmospheric pressure.

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MARTIN. Chlorine and Chlorine Products.

CHAPTER XVII

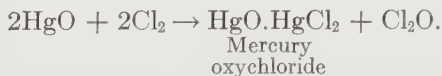
THE OXIDES AND OXYGEN ACIDS OF THE HALOGENS

303. **Oxides and Oxyacids of Chlorine.** — The following oxides and oxyacids of chlorine are known:

<i>Oxides</i>	<i>Oxyacids</i>
Chlorine monoxide, Cl_2O	$\longleftrightarrow \text{HClO}$, Hypochlorous acid [HClO_2], Chlorous acid
Chlorine dioxide, ClO_2	HClO_3 , Chloric acid
Chlorine heptoxide, Cl_2O_7	$\longleftrightarrow \text{HClO}_4$, Perchloric acid

Chlorine and oxygen do not combine directly, but their union can be accomplished in the presence of a basic oxide. As a rule, the oxygen compounds of chlorine are unstable, some of them being dangerously explosive: *e.g.*, Cl_2O and ClO_2 . Perchloric acid is the most stable of the oxyacids of chlorine. The oxygen compounds of chlorine are powerful oxidizing agents. Thus, Cl_2O , ClO_2 , HClO_3 , and HClO_4 cause such substances as paper and wood to inflame. HClO_2 is known only in solution; salts (chlorites) of the acid have been prepared.

304. **The Oxides of Chlorine.** — **Chlorine monoxide**, Cl_2O , may be obtained by passing dry chlorine over dry and recently ignited mercuric oxide, which is contained in a tube cooled with ice and salt:



The gas may be liquefied in a tube surrounded by an ice-salt mixture.

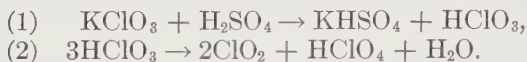
Chlorine monoxide is a brownish-yellow gas, condensing to a dark-yellow liquid. The gas has a peculiar penetrating odor and irritates the eyes. This oxide is very explosive, many oxidizable substances catching fire in its presence:



Chlorine monoxide is the anhydride of hypochlorous acid, being readily soluble in water:



Chlorine dioxide, ClO_2 , is formed when powdered potassium chlorate is added gradually to concentrated sulfuric acid [Care!]:

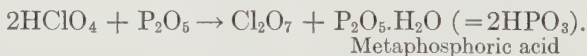


Chlorine dioxide is a heavy gas with a dark-yellow color, which condenses to a dark-red liquid. The compound must be handled with great care as it is very liable to explode. It can be distilled if every trace of organic matter is absent. It is, of course, a powerful oxidizing agent. Thus, a mixture of KClO_3 and sugar ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) may be ignited by adding a drop of concentrated sulfuric acid. [*Care! Avoid friction in preparing the mixture.*]

A mixture of KClO_3 and hydrochloric acid is a powerful oxidizing agent, both ClO_2 and Cl_2 being formed. The chemical change is represented approximately as follows:



Chlorine heptoxide, Cl_2O_7 , can be prepared by slowly adding perchloric acid to cool phosphoric anhydride (P_2O_5) and then distilling off the heptoxide (about 82°). The acid is dehydrated:



Chlorine heptoxide is a colorless oily liquid, boiling at 82° . Under certain conditions the substance explodes with great violence. It is the anhydride of perchloric acid (HClO_4):



THE OXYGEN ACIDS OF CHLORINE

305. **Hypochlorous Acid.** — We have already seen that a solution of hypochlorous acid may be obtained by dissolving chlorine monoxide in water:



When chlorine interacts with water, hydrochloric acid is also formed:



On a large scale, hypochlorous acid is prepared by the interaction of bleaching powder or chloride of lime (CaOCl_2) and an acid:



Other mineral acids, *e.g.*, phosphoric acid, may be used, but not enough to liberate HCl from CaCl_2 , for free HClO would interact with HCl to form chlorine. When bleaching powder is suspended in ice-cold water and the salt decomposed by passing in carbon dioxide, a solution containing hypochlorous acid is obtained:



The salts of HClO (*hypochlorites*) are decomposed by carbonic acid, hypochlorous acid being liberated.

Anhydrous hypochlorous acid has never been prepared, for it is so unstable that only the dilute solutions can be distilled without decomposition. Hypochlorous acid is a powerful oxidizing and bleaching agent. When aqueous solutions of hypochlorous acid are exposed to the light, they decompose thus:



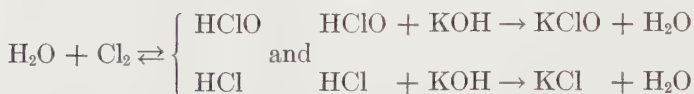
HClO has a great tendency to oxidize into acids richer in oxygen. The structural formula is often written $\text{H}-\text{O}-\text{Cl}$ or $\text{H}:\ddot{\text{O}}:\ddot{\text{Cl}}:$. A concentrated solution of the acid thus undergoes "self-oxidation." Not only is the acid very unstable, but very weak.

306. Hypochlorites. — Some of the salts of hypochlorous acid are very important, bleaching powder being the most important of all. The hypochlorites of sodium and of potassium are also important. As a rule, pure hypochlorites are not required for technical purposes. The hypochlorites are excellent oxidizing and bleaching agents.

In the preparation of hypochlorites, the solutions of the respective hydroxides (or alkali carbonates) must be cold and dilute:



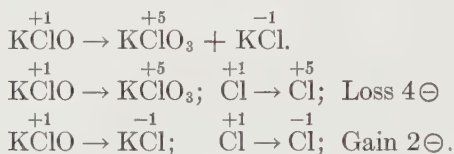
We may regard chlorine as first interacting with water to form hypochlorous and hydrochloric acids and the latter are then neutralized by the alkali hydroxide:



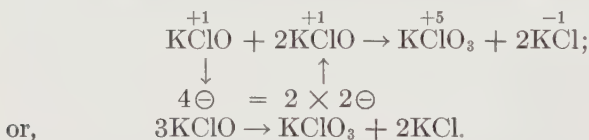
In case the solutions are hot, chlorates are formed:



To show the simultaneous change of potassium hypochlorite to potassium chlorate and potassium chloride, the equation may be written by the electron method as follows:



Therefore, one molecule of potassium hypochlorite is oxidized to the chlorate and two molecules reduced to the chloride:



This type of change comes under the head of "compensating valence changes"; it is "self-oxidation" of potassium hypochlorite to the chlorate.

Hypochlorites also may be obtained by electrolysis. Thus, if a solution of NaCl be subjected to electrolysis, the chlorine will diffuse and interact with NaOH to form NaClO and NaClO₃ unless the substances are kept apart. Under suitable conditions the formation of chlorate is avoided.

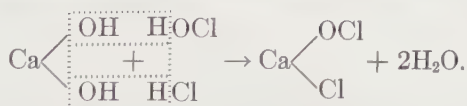
A solution of KClO and KCl is called *eau de Javelle*, (Javelle water), because it was first prepared at Javelle, a suburb of Paris, in 1792. A solution of the corresponding sodium salt is called *Labarraque's solution* (Labarraque, 1820). The hypochlorite is the active component in both solutions. Eau de Labarraque is cheaper than eau de Javelle. At the present time "Javelle water"

contains the sodium salts. Dakin's and Carrel's solutions, which are similar to Javelle water, were used extensively during the Great War for cleansing deep wounds.

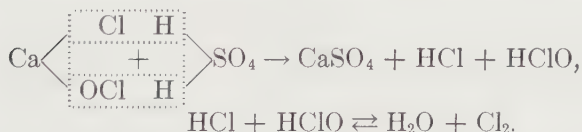
307. **Bleaching Powder or Chloride of Lime, CaOCl_2 .** — This highly important substance was prepared by Tennant in 1799, who absorbed chlorine in dry calcium hydroxide (slaked lime). Bleaching powder then sold for £140 per ton. It is prepared on a very large scale by conducting chlorine gas into a series of large rooms, over the floors of which slaked lime is spread:



Bleaching powder is a yellowish white solid. High-grade specimens contain 36 per cent of "available chlorine." It is usually regarded as a *mixed salt* (245) — half chloride and half hypochlorite; that is, it contains one metal in union with two different acid radicals, or one molecule of each of two monobasic acids may be regarded as neutralizing one molecule of calcium hydroxide:



When treated with strong acids, it yields chlorine:



When the substance is exposed to the air, it absorbs H_2O and CO_2 , forming hypochlorous acid (or its anhydride), which gives it its characteristic odor. The material should be preserved, therefore, in air-tight containers.

When bleaching powder is decomposed by a limited amount of a strong acid, much HClO is formed and a relatively small amount of HCl . According to the ionic theory, hypochlorous acid is weak and therefore mostly molecular, while hydrochloric acid is highly ionized.

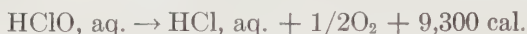
Bleaching powder is used extensively for bleaching vegetable fibers for the textile and paper industries; also as a disinfectant. It is cheaper than the hypochlorites of sodium and of potassium. Hypochlorous acid, chlorine, and oxygen may be obtained from

bleaching powder. The addition of a catalyst, such as $\text{Co}(\text{OH})_2$, hastens the evolution of oxygen:



308. Bleaching. — Chlorine and hypochlorites are used on a large scale in bleaching. The former was first employed by the French chemist Berthollet (1785), while the first hypochlorite for bleaching was prepared at Javelle in 1789.

Vegetable fiber (cotton, linen, or wood pulp) may be bleached by first saturating the material with a solution of bleaching powder and then passing it into a bath containing a dilute mineral acid, which liberates hypochlorous acid (Fig. 112). The latter then decomposes, yielding oxygen and energy:



Hypochlorous acid is a more active oxidizing agent than is free oxygen, for when it decomposes a great deal of energy is liberated.

Vegetable fiber, after appropriate preliminary treatment, also is bleached by saturating the material with a solution of bleaching powder and then piling it loosely in the air. Carbonic acid interacts with the bleaching powder, yielding hypochlorous acid. It should be noted that chlorine does not act directly as a bleaching agent.

309. Chlorous Acid, HClO_2 . — A solution of chlorous acid may be prepared by treating a solution of barium chlorite, $\text{Ba}(\text{ClO}_2)_2$, with sulfuric acid and then filtering off the precipitate of barium sulfate:

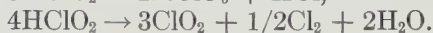


The anhydrous acid is unknown, for the compound is very unstable. Its anhydride, Cl_2O_3 , is also unknown.

When a solution of potassium hydroxide is treated with a solution of chlorine dioxide, a mixture of potassium chlorite and potassium chlorate is obtained:



In this reaction ClO_2 plays the part of a *double anhydride*. The acid may decompose according to the following equations:



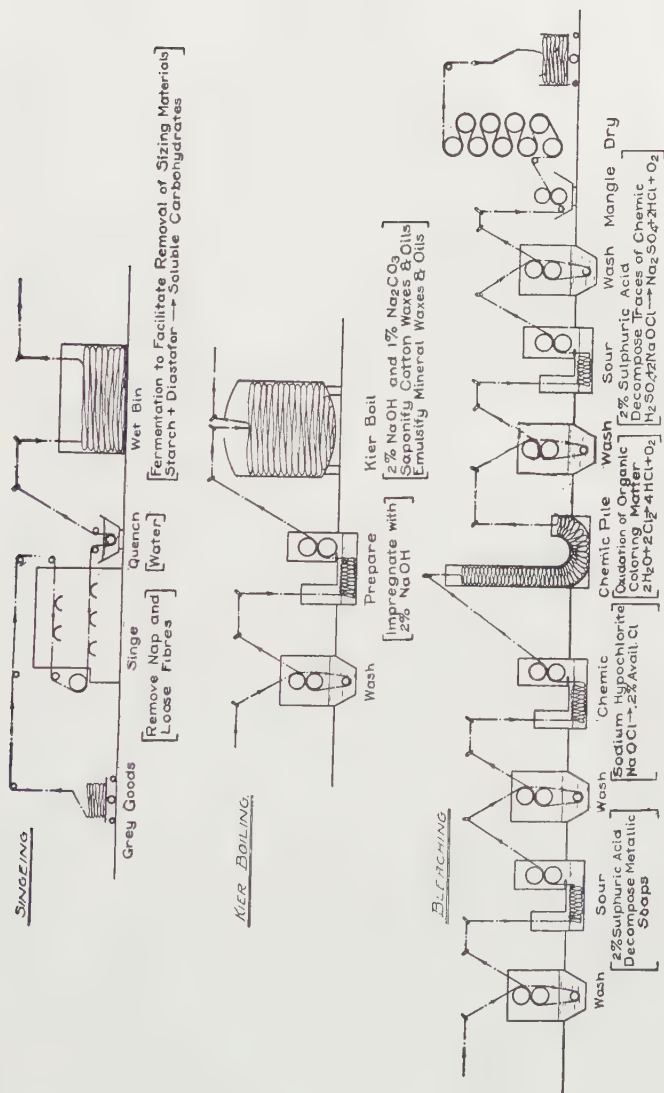


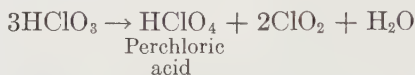
Fig. 112. Diagram Illustrating the Process of Bleaching Vegetable Fiber.
 Courtesy, The United States Finishing Co.

Chlorites are unstable oxidizing agents and are liable to start combustion or to explode when rubbed with a combustible material such as sulfur.

310. **Chloric Acid, HClO_3 .** — Chloric acid is the most important member of the series of the oxyacids of chlorine. It can be prepared in the laboratory by treating certain chlorates with mineral acids. Thus, when a solution of barium chlorate, $\text{Ba}(\text{ClO}_3)_2$, is decomposed by sulfuric acid, a solution of chloric acid is obtained:

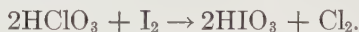


The BaSO_4 is filtered off and the solution evaporated *in vacuo* over H_2SO_4 . When the residue is concentrated beyond 40 per cent of HClO_3 , or when the solution is heated, the acid decomposes:

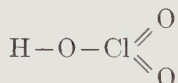


Chloric acid is therefore very unstable, being a powerful oxidizing agent. Like concentrated nitric acid, it may set fire to straw, etc. (Compare the two acids in other respects.)

Chloric acid oxidizes iodine to iodic acid, or iodine displaces chlorine in this reaction:



The graphic formula for HClO_3 is often written thus:



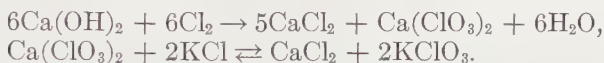
It is analogous to nitric acid (HNO_3).

311. **Chlorates.** — Chlorates, the salts of chloric acid, are very important compounds, particularly potassium chlorate, KClO_3 , and sodium chlorate, NaClO_3 . We have already seen that chlorates may be obtained by the electrolysis of an alkali chloride. This process has greatly reduced the price of potassium chlorate. Chlorates also are formed when hot, concentrated solutions of alkali hydroxides are treated with chlorine:



When this reaction is carried out, KClO is first formed, and then oxidizes to form KClO_3 (write equations). This would be a very

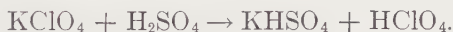
wasteful process for the large-scale production of KClO_3 , for five-sixths of the KOH is transformed into KCl . This great waste is avoided by first substituting calcium hydroxide for potassium hydroxide and then adding potassium chloride:



CaCl_2 is very soluble. Potassium chlorate also is produced by the electrolysis of a solution of KCl at a temperature of $60\text{--}70^\circ$, the anode and cathode products being allowed to mix.

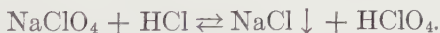
Chlorates are powerful oxidizing agents, many of them being dangerously explosive; hence the use of KClO_3 in the manufacture of matches, flash-light powders, oxygen, and fire-works.

312. Perchloric Acid, HClO_4 .—Perchloric acid may be obtained by treating potassium perchlorate, KClO_4 , with strong sulfuric acid:



When the mixture of the salt and acid is distilled under reduced pressure, perchloric acid is obtained as a colorless liquid.

Richards and Willard prepare perchloric acid by treating a saturated solution of sodium perchlorate with hydrochloric acid (sp. gr. 1.2):



The liquid is decanted off, and carefully distilled under reduced pressure. Under a pressure of 18 mm., the acid boils at 16° . It combines energetically with water to form several hydrates: *e.g.*, $\text{HClO}_4 \cdot \text{H}_2\text{O}$. Perchloric acid is a powerful oxidizing agent. Thus, it inflames paper and wood and causes serious burns when brought in contact with the skin. In dilute solutions, however, it does not exhibit oxidizing properties. Its anhydride is chlorine heptoxide, Cl_2O_7 . Concentrated perchloric acid is used in analytical chemistry.

The salts of perchloric acid are called **perchlorates**. They are the most stable of the salts of the oxygen acids of chlorine. These salts are soluble in water and dissociate to form the perchlorate-ion, ClO_4^- :



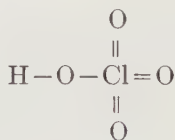
Potassium perchlorate may be obtained by heating potassium chlorate just above its melting point:



When heated to a higher temperature, oxygen is freely formed. Potassium perchlorate is much less soluble in water than is potassium chloride, so the two salts may be separated by crystallization. Potassium perchlorate is almost insoluble in 95 per cent alcohol, containing 0.2 per cent of perchloric acid, and it may be employed, therefore, in the estimation of potassium. Perchloric acid and perchlorates can be prepared by the electrolysis of chloric acid and chlorates respectively.

Perchlorates, like chlorates, nitrates, and acetates, are soluble in water. KClO_4 and RbClO_4 are sparingly soluble in water, but practically insoluble in absolute alcohol.

The structural formula for HClO_4 is usually written thus:



In this compound chlorine has a maximum valence of +7. Perchlorates with sulfuric acid yield perchloric acid, while chlorates yield the explosive yellow gas, chlorine peroxide, ClO_2 .

313. Oxygen Acids of Bromine. — No oxides of bromine are known, but *hypobromous acid* (HBrO) and *bromic acid* (HBrO_3) are well known, being similar to the corresponding compounds of chlorine.

The salts of these acids may be prepared by methods similar to those used for the corresponding chlorine compounds. When bromine is added to cold, dilute potassium hydroxide solution, potassium hypobromite is formed, and when the solution is heated potassium bromate is formed:



Bromic acid oxidizes iodine to iodic acid, which shows that the affinity of iodine for oxygen is greater than that of bromine:

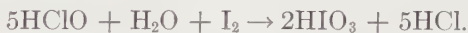


314. **The Oxygen Acids of Iodine.** — *Hypoiodous acid* (HIO), *iodic acid* (HIO₃), and *periodic acid* (HIO₄·2H₂O) are also known. Iodic oxide, I₂O₅, may be obtained as a white powder by heating iodic acid:



It is the anhydride of iodic acid, just as N₂O₅ is the anhydride of nitric acid.

The iodates of the alkali metals may be prepared by treating a hot solution of an alkali with finely divided iodine (see Chlorates and Bromates. Write the equation). Iodic acid may be prepared by oxidizing iodine:



In practice, chlorine is passed through iodine suspended in water.

Sodium iodate (NaIO₃) and sodium periodate (NaIO₄) occur in Chile saltpeter (491).

Normal periodic acid, HIO₄, is not known; but the hydrate, H₅IO₆ or HIO₄ + 2H₂O, is formed by decomposing silver periodate with bromine, or by the electrolytic oxidation of iodic acid. Salts of this acid are known: *e.g.*, Ag₅IO₆ and Na₂H₃IO₆. Indeed, many complex *periodates* are known, all of which are based upon the hypothetical periodic anhydride I₂O₇ (see Cl₂O₇).

EXERCISES

1. Give the preparation and the properties of the oxides of chlorine, and show their relation to the oxygen acids of the element.

2. Outline two methods for the preparation of an aqueous solution of hypochlorous acid. Show by chemical equations the products which may be formed when the acid decomposes.

3. How may hypochlorites be prepared? Point out their properties and technical importance.

4. Outline the large-scale production of bleaching powder. Give proof that it is a mixed salt. Explain fully how hypochlorites act as bleaching and disinfecting agents.

5. Calculate the percentage of "available chlorine" in a specimen of pure bleaching powder.

6. How would you prepare chlorous acid solution from barium chlorite, and chloric acid from barium chlorate? What are the chemical properties of these acids? How would you prepare potassium chlorate from KOH? from KCl? What are the properties and uses of chlorates?

7. Show how you would prepare potassium perchlorate from potassium chlorate, and perchloric acid from potassium perchlorate?

8. Potassium perchlorate is practically insoluble in 95 per cent alcohol

containing 0.2 per cent of perchloric acid. Explain fully why the presence of the acid lowers the solubility of the salt.

9. (a) A certain weight of lithium perchlorate was heated until completely decomposed into lithium chloride and oxygen, the weight of the latter being 1.50968 g. Calculate the weight of the perchlorate heated and the weight of the chloride formed.

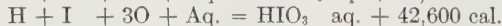
(b) The lithium chloride obtained in (a) was converted into silver chloride, and 2.54455 g. of silver were obtained from the latter compound. From the weights of the oxygen and the silver (given the atomic weight of oxygen as 16) calculate to the second decimal place the atomic weight of silver.

10. (a) A certain weight of lithium chloride (from LiClO_4) was converted into silver chloride, and the ratio of the two weights $\left[\frac{\text{LiCl}}{\text{AgCl}}\right]$ was found to be 0.2958. Given the atomic weight of silver as 107.88 and chlorine as 35.46, calculate to the second decimal place the atomic weight of lithium.

(b) By experiment the ratio by weight of lithium chloride and silver $\left[\frac{\text{LiCl}}{\text{Ag}}\right]$ was found to be 0.39299. Find the atomic weight of lithium.

11. Explain, in terms of the ionic theory, (1) why bleaching powder and a moderately concentrated solution of H_2SO_4 interact to form HCl , HClO , and Cl_2 ; and (2) why bleaching powder and H_2CO_3 interact to form HClO and no appreciable concentration of HCl . (Note. — $\text{CaCl}(\text{ClO})$ ionizes thus: $\text{CaCl}(\text{ClO}) \rightleftharpoons \text{Ca}^{++} + \text{Cl}^- + \text{ClO}^-$. H_2SO_4 and HCl are strong acids, whereas HClO and H_2CO_3 are weak.)

12. The heats of formation of chloric, bromic, and iodic are as follows:



What is the order of stability of these acids?

13. Will free iodine displace chlorine from chlorates and bromine from bromates? Will free bromine displace chlorine from chlorates?

14. Write equations showing the action of an excess of hydrochloric acid upon bleaching powder.

15. Write equations to show the effect of bromine upon (1) barium hydroxide; (2) a cold, dilute solution of potassium hydroxide; (3) a hot, concentrated solution of calcium hydroxide; (4) the action of chlorine dioxide upon sodium hydroxide; and (5) how calcium chlorate may be transformed into potassium chlorate.

16. Outline tests which would enable one to differentiate the following acids: hydrochloric, hypochlorous, chloric, and perchloric.

17. Justify the following statement: "The more oxygen the oxyacids of chlorine contain, *i.e.*, the higher the positive valence number of the chlorine, the more stable and the more strongly acid they are."

READINGS AND REFERENCES

FRIEND. Textbook of Inorganic Chemistry, Vol. VIII.

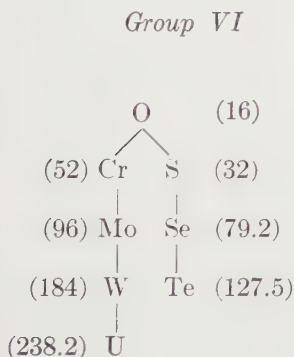
ROSCOE AND SCHORLEMMER. Treatise on Chemistry, Vol. I, pp. 344–372.

SMITH-KENDALL. Inorganic Chemistry, Chap. XXII.

CHAPTER XVIII

THE SULFUR FAMILY. HYDROGEN SULFIDE

315. **Relationships and General Characteristics.** — Group VI of the Periodic System contains two families of elements: Chromium and related metals (Chap. XXXVI) constitute Sub-group A; while Sub-group B contains *sulfur*, *selenium*, and *tellurium*, being known as the Sulfur Family. Oxygen is sometimes regarded as an element forming a connecting link between the chromium and sulfur families, as shown in the accompanying diagram.



Since oxygen is much more closely related to sulfur than to the elements of the chromium family, it may be properly considered as a member of the sulfur family. The elements of Sub-group A have pronounced metallic characteristics, or are principally base-forming, while the elements of Sub-group B are acid-forming. In general, the basic nature of the element increases with increase in atomic weight. In the sulfur family signs of a basic character first appear in tellurium.

Chromium, molybdenum, and tungsten (W) form anhydrides which are analogous to the trioxides of sulfur and of tellurium (no trioxide of selenium is known):

<i>Anhydride</i>	<i>Acid</i>	<i>Salt</i>
CrO ₃	Chromic, H ₂ CrO ₄	Potassium chromate, K ₂ CrO ₄
MoO ₃	Molybdic, H ₂ MoO ₄	Potassium molybdate, K ₂ MoO ₄
WO ₃	Tungstic, H ₂ WO ₄	Sodium tungstate, Na ₂ WO ₄
SO ₃	Sulfuric, H ₂ SO ₄	Potassium sulfate, K ₂ SO ₄
TeO ₃	Telluric, H ₂ TeO ₄	Potassium tellurate, K ₂ TeO ₄

The elements of Group VI have a multiple valence, which varies from 2 to 6: *e.g.*, H₂S, SeO₂, TeO₃, SF₆. In H₂S the valence of

sulfur is -2 , while in SF_6 it is $+6$. The sulfur atom is therefore regarded as having 6 valence (outer) electrons.

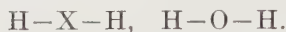
The members of Sub-group B form compounds with metals, such as:



When these compounds are decomposed by acids, hydrides, H_2X , are formed (oxides yield H_2O), for example:



H_2S , H_2Se , and H_2Te are analogous to water:



The hydrides of sulfur, selenium, and tellurium are colorless, poisonous gases, and their aqueous solutions display weakly acidic properties. Sulfides, selenides, and tellurides are closely related compounds. All the elements of the sulfur family show allotropy.

Some of the properties of these elements are summarized in the table below.

THE PROPERTIES OF THE ELEMENTS OF THE SULFUR FAMILY

Property	Oxygen, O	Sulfur, S	Selenium, Se	Tellurium, Te
Atomic weight.....	16.00	32.06	79.2	127.5
Melting point.....	-227°	113°	217°	452°
Boiling point.....	-183°	445°	680°	1290°
Density (solid).....	1.43	1.96–2.06	4.26–4.80	6.015–6.27
Color of solid.....	Pale blue	Yellow	Reddish-brown	Silver-gray to black
Hydrides XH_2	H_2O	H_2S	H_2Se	H_2Te
Oxides.....	SO_2	SeO_2	TeO_2
	SO_3	TeO_3
	O_2O_2 (or O_3)
Oxygen acids.....	H_2SO_3	H_2SeO_3	H_2TeO_3
	H_2SO_4	H_2SeO_4	H_2TeO_4

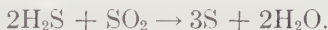
SULFUR. S = 32.06

316. History and Occurrence.—Sulfur was one of the few elements known to the ancients, since it occurs in the free state. It was formerly called “brimstone.” Thus, we find in Genesis that “the Lord rained upon Sodom and upon Gomorrah brimstone and fire.” The element also is mentioned in the writings of Homer. Sulfur was burned in ancient times for the purpose of fumigation;

and according to Paracelsus it was one of three constituents of the human body, salt and mercury being the others. The alchemists believed sulfur to be the principle of fire, which accounts for the saying: "Where there is fire and heat, there is sulfur."

Sulfur occurs abundantly and widely distributed in nature. In the free state it is found in volcanic districts of Italy, Sicily, Iceland, Mexico, and other countries. Native sulfur is especially abundant in Sicily and in the United States, Louisiana and Texas being noted for their large and remarkably pure deposits of the element. Before 1900, Sicily furnished about 90 per cent of the world's supply of sulfur; but in 1918 the United States mined 1,353,000 tons, which was 65 per cent more than the world's production in 1913. In 1926 the domestic production of sulfur was over 2,000,000 tons.

The precise way in which native sulfur is formed is not known. Volcanic gases, such as those of Vesuvius and of Mount Aetna, generally contain sulfur dioxide and hydrogen sulfide, and when these moist gases interact they decompose, sulfur being deposited. Deposits of this type are being formed at the present time. The formation of sulfur may be shown by bringing mouth to mouth two bottles, one filled with hydrogen sulfide and the other with sulfur dioxide:



Much of the native sulfur may have been formed by the reduction of calcium sulfate or gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.

Sulfur in the combined state is much more abundant and widely distributed than is native sulfur. It occurs principally as *sulfides* and *sulfates*. Many sulfide minerals are of great industrial importance, such as iron pyrites, copper pyrites, zinc sulfide or blende, lead sulfide, or galena, and mercuric sulfide, or cinnabar. Iron pyrites has somewhat the appearance of gold; therefore it is appropriately called "fool's gold." Hydrogen sulfide, or sulfuretted hydrogen, is present in the so-called sulfur waters and in certain volcanic gases. The water from one of the sulfur springs in Iceland is said to be ejected to a height of several feet, accompanied by a hissing noise.

Sulfates are found in very large quantities, both in the crust of the earth and in sea-water. Among these compounds some of the most important are calcium sulfate or gypsum, barium sulfate or heavy spar, strontium sulfate or celestite, and magnesium sulfate or Epsom salt. Millions of tons of gypsum are mined annually;

it is used in agriculture, in the manufacture of plaster of Paris and wall plaster, and as a filler of paper.

SOME IMPORTANT MINERALS CONTAINING SULFUR

Sulfides	Sulfates
Iron pyrites..... FeS_2	Gypsum..... $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
Galena..... PbS	Gypsum anhydrite.... CaSO_4
Zinc blende..... ZnS	Celestite..... SrSO_4
Chalcopyrite..... CuFeS_2	Barite..... BaSO_4
Cinnabar..... HgS	Epsom salt..... $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$
Stibnite..... Sb_2S_3	Kieserite..... $\text{MgSO}_4 \cdot \text{H}_2\text{O}$

Sulfur compounds are found broadly distributed in the vegetable and animal kingdoms. Sulfur is therefore an essential constituent of certain forms of life. Sulfur compounds are present in garlic, onions, hair, wool, the blood, bile, etc. About one per cent of the element is contained in all the albuminous substances, which are so important in the animal body. Proteins are the only source of sulfur in a form suitable for use by the tissues. Sulfur is a constituent of *hemoglobin*, each red blood-cell containing billions of molecules of this complex substance, the molecular weight of which is very great. Sulfur also is present in petroleum and in coal. The element is a great nuisance in fuel, for it injures boilers and grate-bars. Likewise, it is very objectionable in iron ores, for it makes iron "red short" — *i.e.*, brittle when hot.

317. Manufacture. — Two main methods are employed in the production of sulfur, namely, the Frasch process and the crude method of Sicily.

In the United States, the **Frasch method** is employed. In Louisiana, there is a deposit of sulfur about 900 feet below clay, rock, and quicksand. The deposit is over half a mile in diameter and is estimated to be many millions of tons, so America no longer has to import sulfur. In Louisiana and Texas, sulfur is extracted by a method worked out by an American chemist, Hermann Frasch (Fig. 113). A boring is made through the overlying material until the beds of sulfur are reached, and then through the opening three or four concentric pipes are driven. Superheated water (165° to 170°) is forced down the outside pipe or pipes, and it melts the sulfur, which runs into the sump at the foot of the well. Compressed hot air is forced to the bottom of the well through the smallest pipe, where it mixes with the sulfur. The mixture of air

and sulfur rises through the pipe surrounding the airpipe, and sulfur is discharged into large vats constructed of boards. The sulfur thus obtained is over 99.5 per cent pure, and the solidified product is used in commerce without further refining. A single well often produces 500 tons of sulfur daily, one well having been known to produce sulfur at the rate of 1,200 tons per day, and the most productive wells are said to have yielded more than 100,000 tons. A single block of the element has contained over 1,000,000 tons.

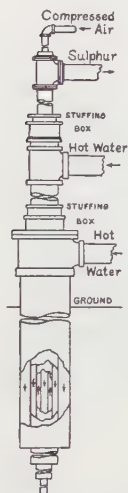


FIG. 113.

In Sicily, sulfur is found mixed with earthy materials called matrix or gangue. The ore is generally heated in kilns ("calceroni"), some of the sulfur burning to furnish the necessary heat. The remaining sulfur melts and is collected in a pool near a tap-hole, from which it is



FIG. 114.

drawn off from time to time into moulds. The method is crude and wasteful.

Of late years, the Gill Kiln, in which coke is used as fuel, has partially displaced the older method.

Commercial Sicilian sulfur is refined by distillation from an iron retort (Fig. 114), the vapor passing into a large chamber, where it condenses, at the beginning, to **flowers of sulfur**. When the chamber becomes heated above the melting point of sulfur, it collects as a liquid which can be drawn off and then cast in slightly conical wooden moulds, and is called **roll sulfur**.

Sulfur is obtained as a by-product in the manufacture of soda by the Leblanc process, being obtained from calcium sulfide waste.

318. Physical Properties. — Sulfur exists in several different forms (see Oxygen and Ozone, Chap. VI).

(1) **Rhombic Sulfur.** Sulfur occurs in nature in large yellow crystals belonging to the rhombic system. This form of sulfur may be obtained by allowing sulfur slowly to crystallize from

solution in carbon disulfide, or by cooling the liquid substance under proper conditions (Fig. 115). Rhombic sulfur has a specific gravity of 2.06, a melting point of 112.8° , and a boiling point of 444.6° ; it is insoluble in water, but soluble in carbon disulfide and in chloride of sulfur (S_2Cl_2). Rhombic sulfur is stable below 96° .

(2) **Monoclinic Sulfur.** Monoclinic (prismatic) sulfur may be prepared when a mass of melted sulfur is allowed to cool at ordi-

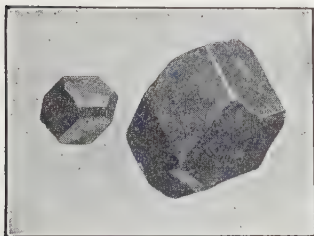


FIG. 115.

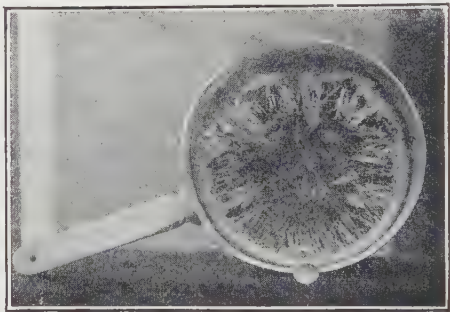


FIG. 116.

nary temperature until a crust is formed on the surface. By breaking the crust and pouring out the sulfur still in the molten condition, the vessel will be lined with long, thin, transparent crystals belonging to the monoclinic system (Fig. 116). The specific gravity of this form of sulfur is 1.96, and it melts at 119.25° ; it is readily soluble in carbon disulfide. Rhombic and monoclinic sulfur are allotropic forms of the element, and their relationship is an interesting one.

Sulfur is *dimorphous*, *i.e.*, there are two distinct crystalline forms. Rhombic sulfur is stable below 96° and monoclinic sulfur is stable between 96° and 119° (its melting point). 96° is called the *transition point*, for these two forms of sulfur are in equilibrium at this temperature:



When monoclinic sulfur is cooled below 96° , it gradually changes to rhombic sulfur, the form occurring in nature.

(3) **Amorphous Sulfur.** When ordinary sulfur is heated to about 113° it melts, forming a mobile pale-yellow liquid; at

160°, the liquid suddenly turns dark-brown in color and becomes quite viscous, the maximum viscosity being reached at about 235°, at which temperature it resembles tar. At higher temperatures it becomes less viscous. If the more mobile liquid obtained at a higher temperature be suddenly chilled by pouring it in a thin stream into cold water, it will form a very viscous, transparent, elastic mass, known as **plastic sulfur** (Fig. 117). It is so viscous that it may be drawn out into long threads. Plastic sulfur is a supercooled liquid. The sulfur is cooled so rapidly that it does not have time to crystallize. On standing, however, it gradually changes to a hard brittle mass, which is in part rhombic sulfur. Solvents have but little action on plastic sulfur, but the crystalline part can be dissolved in CS₂.



FIG. 117.

According to Alexander Smith, there are two liquid forms of sulfur, known as S_λ and S_μ:



With rising temperature, the second variety is formed at the expense of the first; but when the liquid is cooled, the reverse change occurs. Both rhombic and monoclinic sulfur yield identical liquids when melted.

(4) **Milk of Sulfur** (*lac sulfuris*). When aqueous solutions of certain compounds rich in sulfur (polysulfides) are acidulated, sulfur separates from the solution, giving it the appearance of milk; hence the name "milk of sulfur." This substance was known to the Arabian Geber and is now used as a medicine. It is very finely divided and consists in part of very small rhombic crystals. The equation for the preparation of milk of sulfur from calcium polysulfide may be written thus:



Recent investigations show that there are other forms of sulfur.

319. Chemical Properties. — Oxygen and sulfur, as we have seen, belong to the same family, so they form many compounds which are analogous — oxides, sulfides, etc.

Some Oxygen Compounds

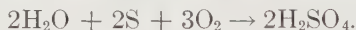
H_2O
 CO_2
 FeO
 As_2O_3
 As_2O_5
 NaOH
 H_3AsO_4 (arsenic acid)

Some Sulfur Compounds

H_2S
 CS_2
 FeS
 As_2S_3
 As_2S_5
 NaSH
 H_3AsS_4 (sulfarsenic acid)

Sulfur, like oxygen, is an active element, particularly at high temperatures. When heated with metals, sulfur behaves very much as does oxygen. All the ordinary metals, except gold and platinum, unite with it to form sulfides, in some cases with the evolution of light (see FeS). Silver tarnishes readily when in contact with sulfur; and when sulfur and mercury are rubbed in a mortar, mercuric sulfide (HgS) is formed.

Sulfur unites with most of the non-metals. When heated in air it burns to form sulfur dioxide (SO_2); with heated carbon, carbon disulfide (CS_2); with chlorine, it forms liquid chlorides (S_2Cl_2 , SCl_2 , SCl_4); with hydrogen, hydrogen sulfide (H_2S). In the presence of moist air, sulfur is slowly oxidized to sulfuric acid:



When sulfur is treated with suitable oxidizing agents, it is converted into sulfuric acid. When sulfur is vaporized, its density varies with change in temperature, due to dissociation (197). The molecules may be octatomic (S_8), diatomic (S_2), or monatomic (S).

Sulfur probably forms more evil-smelling compounds than does any other element. These are represented by hydrogen sulfide, the sulfur compounds of the onion and garlic, and the *mercaptans*, or *sulfur alcohols*, such as CH_3SH and $\text{C}_2\text{H}_5\text{SH}$. These alcohols are analogous to methyl alcohol (CH_3OH) and ethyl alcohol ($\text{C}_2\text{H}_5\text{OH}$). It is thus seen that an atom of sulfur may take the place of one of oxygen.

320. Uses of Sulfur. — Crude sulfur is used chiefly in vineyards to destroy fungi; for manufacturing sulfuric acid, sulfur dioxide, sulfurous acid, bisulfite solutions, carbon disulfide, and ultramarine. Refined sulfur is used for gunpowder, matches, fireworks, and for the manufacture of vulcanized rubber (vulcanite).

During the Great War there was a large demand for sulfur for the manufacture of "mustard gas" (275).

SELENIUM (Se = 79.2) AND TELLURIUM (Te = 127.5)

Selenium and tellurium belong to the same family as oxygen and sulfur. Selenium is very closely related to sulfur, and tellurium closely resembles the latter in its compounds.

321. Selenium. — *Selenium* (Greek, meaning *the moon*) was discovered by Berzelius in 1817, who found it in the deposit from sulfuric acid chambers. The element occurs in certain sulfides and in some specimens of native sulfur. Selenium is obtained as a by-product in the electrolytic refining of copper and lead.

Selenium, like sulfur, may be prepared in several allotropic modifications. The element is about as closely related to sulfur as chlorine is to bromine and iodine.

When selenium is carefully annealed, it conducts electricity, its conductivity increasing on exposure to light. Graham Bell made use of this property of the element in the construction of a *photophone*, and Joel Stebbins (1914) constructed a delicate *photometer* for measuring the relative intensity of the light of stars. By employing selenium, it is possible to telegraph pictures and drawings.

Selenium is used to color glass red; it neutralizes the greenish tint of ferrous iron, and can be employed instead of manganese dioxide in decolorizing glass. In 1918, when the supply of MnO_2 was limited, 20,000 pounds were used in the United States for this purpose. The supply of selenium is now above the demand.

322. Tellurium. — This element was discovered by Müller von Reichenstein in 1782. The discovery was confirmed (1798) by Klaproth, who named the element *tellurium* (Lat. *tellus*, the earth). The element occurs in small quantities in the free state, but it is generally found in combination with metals. Thus, *sylvanite* is a telluride of silver and gold (AgAuTe_2). Tellurium is obtained as a by-product in the electrolytic refining of copper and lead, being extracted from the anode sludge. The United States has facilities for the annual production of about 125,000 pounds. Tellurium does not resemble sulfur closely; it resembles antimony in appearance, being a silver-gray, metallic-looking substance. Its sp. gr. is about 6.26, and it is brittle. Tellurium is not of much commercial importance, but there is a small demand for use in radio-sets.

HYDROGEN SULFIDE, H_2S

323. Occurrence. — Hydrogen sulfide, or sulfuretted hydrogen, occurs in certain volcanic gases and in the so-called sulfur waters,

such as those of Harrogate. It is formed when various organic bodies (proteins) undergo putrefactive decomposition. Thus, the offensive smell of decomposing eggs is due in part to this gas. Many sulfides of metals, a source of hydrogen sulfide, are found in nature.

324. Preparation. — Hydrogen sulfide is best prepared by treating certain sulfides with dilute acids. The cheapest sulfide available is ferrous sulfide:



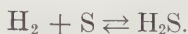
The preparation may be conveniently carried out by employing a Kipp apparatus (122). Dilute sulfuric acid may be substituted for hydrochloric acid; but an oxidizing acid, such as nitric, cannot be used.

The gas thus obtained is not pure, for ferrous sulfide always contains more or less metallic iron. To obtain the pure gas, antimony trisulfide may be employed:



H_2S may be dried by passing it through a tube containing P_2O_5 .

It is interesting to know that hydrogen and sulfur will combine, when heated, to form hydrogen sulfide. At 310° , the union is nearly complete, but about 7 days are required to complete the change:



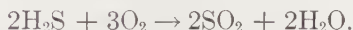
325. Physical Properties. — Hydrogen sulfide is a colorless gas possessing a sweetish taste and a most offensive odor, similar to that of rotten eggs. The gas is a little heavier than air (sp. gr., 1.18). It may be readily condensed to a colorless liquid, the C.T. being 100.4° and the C.P. 89 atmos. The liquid boils at -60° . At 15° , 3.23 vols. of hydrogen sulfide are soluble in 1 vol. of water. The gas may be expelled completely by boiling its aqueous solution.

When hydrogen sulfide is inhaled, it acts as a powerful poison. One part of the gas in 200 parts of air is fatal to mammals; and small animals such as birds are more sensitive. Very dilute chlorine gas, obtained by sprinkling bleaching powder on a towel moistened with acetic acid, may be used as an antidote.

326. Chemical Properties. — Hydrogen sulfide is not a very stable compound, for it dissociates when heated:



This may be proved by holding a white porcelain dish in the flame of burning hydrogen sulfide. Sulfur (yellow), formed in the interior of the flame by dissociation, condenses upon the cold surface of the dish before it has a chance to undergo oxidation. The gas burns in air with a bluish flame, forming sulfur dioxide and water vapor:



All the metals in the electromotive series from the most active down to and including silver interact with hydrogen sulfide to form sulfides. Thus, silver tarnishes when exposed to even small quantities of H_2S .

As hydrogen sulfide is an unstable compound, it is a good reducing agent. Thus, we have already seen that it reduces sulfur dioxide to sulfur (316). Sulfuric acid is not a suitable drying agent for hydrogen sulfide, for the latter reduces the former:



To put it another way, H_2SO_4 oxidizes H_2S , for the latter loses hydrogen. A solution of ferric chloride may be reduced to ferrous chloride by passing H_2S through it:



(Write this equation by the electron method.)

327. Chemical Properties of a Solution of Hydrogen Sulfide. — The solution of H_2S in water is a very feeble acid, sometimes called **hydrosulfuric acid**. The compound ionizes to a very slight extent:



Hydrosulfide-ion (SH^-) is less dissociated than is water, so the concentration of sulfide-ion ($\text{S}^{=}$) is exceedingly low.

A solution of hydrogen sulfide may be used to neutralize bases:



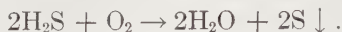
A solution of NaSH is slightly alkaline in reaction. By treating a mol of NaSH with one of NaOH and evaporating off the water, sodium sulfide is obtained:



A solution of Na_2S is strongly alkaline. Sodium sulfide is a salt formed by the interaction of an active base (NaOH) and a weak

acid (H_2S). In general, such a salt is hydrolyzed to some extent by water (257).

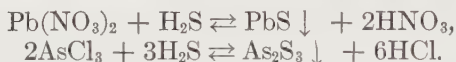
Free oxygen displaces sulfur from hydrogen sulfide:



When an aqueous solution of hydrogen sulfide stands for a long time, sulfur is slowly precipitated.

328. Sulfides. — We have just seen that the aqueous solution of hydrogen sulfide is a feeble dibasic acid. Sulfides may be formed by a number of different methods:

- (1) *By synthesis:* $\text{Fe} + \text{S} \rightarrow \text{FeS}$.
- (2) *By the interaction of a base and hydrogen sulfide* (327).
- (3) *By treating solutions of certain salts with hydrogen sulfide:*



329. Uses of Hydrogen Sulfide. — Hydrogen sulfide is used for separating the metals into groups, for the recognition of certain metals, and as a reducing agent; it is one of the most valuable reagents known to the analyst. *By the use of hydrogen sulfide as a reagent the metals may be separated into three general groups:*

(I) **Metals the sulfides of which are practically insoluble in dilute acids.** These metals are precipitated by hydrogen sulfide in the presence of dilute acids (about 0.3 N). They are the metals of the Copper-Tin Group, including the Copper Sub-group: Hg, Bi, Pb, Cu, Cd (sulfides insoluble in yellow ammonium sulfide); and the Tin Sub-group: As, Sb, Sn (sulfides soluble in yellow ammonium sulfide).

The precipitate may consist of: HgS , Bi_2S_3 , PbS , CuS , CdS , As_2S_3 , As_2S_5 , Sb_2S_3 , Sb_2S_5 , SnS , SnS_2 . Ag_2S (black) is also precipitated by H_2S in the presence of nitric or sulfuric acid (see Hydrochloric Acid).

(II) **Metals not precipitated by hydrogen sulfide in acid solution, but precipitated by ammonium sulfide, $(\text{NH}_4)_2\text{S}$,** which may be prepared by treating ammonium hydroxide with hydrogen sulfide. These metals are: Fe, Cr, Al, Ni, Co, Mn, Zn.

The precipitate may consist of: FeS , $\text{Cr}(\text{OH})_3$, $\text{Al}(\text{OH})_3$, NiS , CoS , MnS , ZnS . These compounds are soluble in dilute acids, such as HCl and H_2SO_4 .

(III) **Metals not precipitated by hydrogen sulfide under any conditions.** These are the Alkali and the Alkaline Earth Metals (76).

The *formation of sulfides* may be illustrated by passing a stream of hydrogen sulfide from a Kipp apparatus successively into four bottles (Fig. 118) containing, respectively, aqueous solutions of (A) lead nitrate, (B) cadmium sulfate, (C) antimony trichloride, and (D) zinc acetate. Lead sulfide (black) is formed in (A):



In (B), yellow cadmium sulfide (CdS) is formed, orange antimony trisulfide (Sb_2S_3) in (C), and white zinc sulfide in (D). (Write the chemical equations to show these reactions; also, write the ionic equations.)

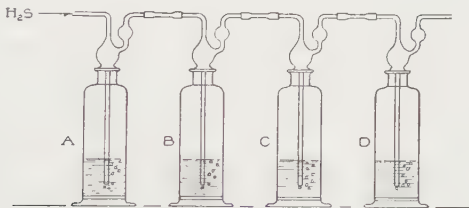
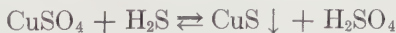


FIG. 118.

On account of the color of certain of the sulfides, H_2S is an important reagent in the recognition of some of the metals.

H_2S readily blackens paper previously treated with a solution of lead acetate. This test and the odor of the gas make its identification easy and certain.

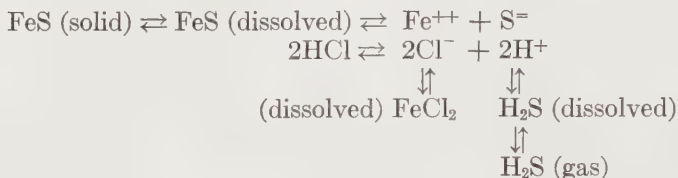
330. Why Hydrogen Sulfide Precipitates Certain Metals. — We have just seen that the sulfides of the metals of the Copper-Tin Group (*e.g.*, CuS) are but slightly soluble in dilute acids, while certain other sulfides (*e.g.*, ZnS and FeS) are readily soluble. This furnishes a basis, therefore, for separating the metals of the Copper-Tin Group from the other metals. The reaction



is reversible, but it requires a very appreciable concentration of the hydrogen-ion to produce any marked effect in driving the action to the left, or in preventing the quantitative precipitation of copper as sulfide.

Hydrogen sulfide is a feeble acid, *i.e.*, the concentration of the sulfide-ion $\text{S}^{=}$ (as well as the hydrogen-ion H^+) is very low. Ferrous sulfide is slightly soluble in water, but despite its low solu-

bility it yields a higher concentration of sulfide-ion than does hydrogen sulfide. When ferrous sulfide is treated with a dilute acid, such as hydrochloric, we have the following equilibria:



The equilibria are continuously displaced forward, due to the fact that slightly ionized and gaseous hydrogen sulfide is formed (255). The formation of H_2S is dependent upon the magnitude of the product of the concentrations of the ions, $[\text{H}^{+}] \times [\text{H}^{+}] \times [\text{S}^{-}]$, or $[\text{H}^{+}]^2 \times [\text{S}^{-}]$. While $[\text{S}^{-}]$ is very low (FeS is almost insoluble in water), $[\text{H}^{+}]$ is very high, due to the ionization of HCl . The product of the ionic concentration is therefore great enough to drive the action forward.

In the case of CuS , however, the solubility of the sulfide is so very low, that the forward action makes but little progress; for the product of the ionic concentrations never reaches sufficient magnitude to form much H_2S . This means that CuS is quantitatively precipitated by the sulfide-ion in the presence of a not too high concentration (0.3 *N* or less) of hydrogen-ion.

EXERCISES

1. Name the elements in Sub-group VI B and give their relationships and general characteristics. How are they related to chromium?
2. Give the occurrence of sulfur, both in the free and the combined state. Mention two ways by means of which sulfur may have been formed in nature. Why do sulfides and certain sulphates occur so abundantly as minerals?
3. Outline the two most important methods for the production of sulfur. How may it be purified?
4. Name and describe three allotropic forms of sulfur. Tell precisely how these forms of sulfur may be prepared. What is the exact relation of rhombic to monoclinic sulfur? Why is plastic sulfur regarded as a super-cooled liquid?
5. Enumerate the chemical properties of sulfur, illustrating with equations. Show its relationship to oxygen.
6. Show the relationship of selenium and tellurium to sulfur, and of their compounds to sulfur compounds.
7. Explain the uses of selenium.
8. Can you explain why hydrogen sulfide occurs in nature? Outline the usual laboratory method of preparing the gas. Why is this gas not

perfectly pure? How would you prepare pure, dry hydrogen sulfide? What objection would there be to passing it through concentrated sulfuric acid or calcium chloride as a drying agent?

9. State the physical properties of hydrogen sulfide. What effect has it upon animals when inhaled? What first aid and antidote would you administer to one who had inhaled an excessive amount of the gas?

10. Outline the chemical properties of hydrogen sulfide and write the equations involved. How would you prove that it is an unstable compound and a good reducing agent? How would you prove that its aqueous solution is a very feeble, dibasic acid?

11. How may the following compounds be prepared: KSH, K_2S , $(NH_4)_2S$ (in solution), $(NH_4)_2S_x$ (in solution), PbS, and FeS?

12. Account for the fact that such substances as CaS, Al_2S_3 , and Cr_2S_3 cannot be prepared in the wet way, *i.e.*, in the presence of water.

13. Explain as fully as you can the action of hydrochloric acid upon FeS, CdS, and Sb_2S_3 .

14. Explain the use of hydrogen sulfide (1) as a reducing agent, and (2) in the analysis of the metals.

15. (a) What volume of normal hydrochloric acid would be required to decompose 21.975 g. of ferrous sulfide?

(b) If 250 cc. of hydrochloric acid were required to decompose 10 g. of ferrous sulfide, what was the normal concentration of the acid?

16. Why does Na_2S hydrolyze to a greater extent than does NaSH?

17. Write the equation by the electron method to show the interaction of H_2S and SO_2 .

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CHAPTER XIX

OXIDES AND OXYGEN ACIDS OF SULFUR

331. **Oxides and Oxyacids of Sulfur.** — The following oxides of sulfur are known:

Sulfur dioxide (sulfurous anhydride)	SO_2
Sulfur trioxide (sulfuric anhydride)	SO_3
Sulfur "sesquioxide" (hyposulfurous anhydride)	S_2O_3
Sulfur heptoxide (persulfuric anhydride)	S_2O_7

The first and second of these oxides are very important.
The oxyacids of sulfur are as follows:

Sulfurous acid	H_2SO_3 , or	$\begin{array}{c} \text{HO} \diagup \text{SO} \\ \text{HO} \diagdown \end{array}$
Sulfuric acid	H_2SO_4 , or	$\begin{array}{c} \text{HO} \diagup \text{SO}_2 \\ \text{HO} \diagdown \\ \text{HO}-\text{SO}_2 \end{array}$
Pyrosulfuric acid	$\text{H}_2\text{S}_2\text{O}_7$, or	$\begin{array}{c} \text{O} \\ \\ \text{HO}-\text{SO}_2 \\ \text{HO}-\text{S}=\text{O} \end{array}$
Hyposulfurous acid	$\text{H}_2\text{S}_2\text{O}_4$, or	$\begin{array}{c} \text{HO}-\text{S}=\text{O} \\ \\ \text{HO}-\text{S}=\text{O} \end{array}$
Caro's acid (permonosulfuric acid)	H_2SO_5 , or	$\begin{array}{c} \text{HO} \diagup \text{SO}_2 \\ \text{HO}-\text{O} \diagdown \end{array}$
Persulfuric acid	$\text{H}_2\text{S}_2\text{O}_8$, or	$\begin{array}{c} \text{HO}-\text{SO}_2-\text{O} \\ \\ \text{HO}-\text{SO}_2-\text{O} \end{array}$
Thiosulfuric acid	$\text{H}_2\text{S}_2\text{O}_3$, or	$\begin{array}{c} \text{HO} \diagup \text{SO}_2, \text{ or} \\ \text{HS} \diagdown \end{array} \quad \begin{array}{c} \text{HO} \diagup \text{S} \\ \text{HO} \diagdown \end{array} \begin{array}{c} \text{S} \\ \parallel \\ \text{O} \end{array}$

In addition to these, the following less important acids are known:

Dithionic acid	$\text{H}_2\text{S}_2\text{O}_6$
Trithionic acid	$\text{H}_2\text{S}_3\text{O}_6$
Tetrathionic acid	$\text{H}_2\text{S}_4\text{O}_6$
Pentathionic acid	$\text{H}_2\text{S}_5\text{O}_6$
Hexathionic acid	$\text{H}_2\text{S}_6\text{O}_6$

"Thio" comes from the Greek word *θεῖον* (*theion*, sulfur).

SULFUR DIOXIDE, SO_2

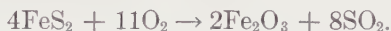
332. **History and Occurrence.** — The ancients knew that when sulfur is burned, a gas with a sharp odor is formed. Fumes of burning sulfur were employed in fumigation. Priestley (1775) first prepared pure gaseous sulfur dioxide. Sulfur dioxide is evolved from active volcanoes, and it also occurs in very small quantities in the atmosphere of cities, formed by the oxidation of sulfur in coal.

333. **Preparation.** — Sulfur dioxide may be prepared by a number of different methods:

(I) **By burning sulfur:**

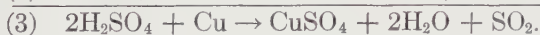
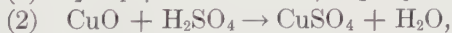


(II) **By roasting or calcining sulfide ores, such as pyrite:**



A large quantity of gas thus prepared has been used in the manufacture of sulfuric acid.

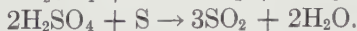
(III) **By reducing concentrated sulfuric acid.** For this purpose, copper, carbon, or sulfur may be employed. For laboratory use, sulfur dioxide is often prepared by treating copper turnings with hot concentrated sulfuric acid. The gas may be collected by the upward displacement of air, or a solution of it may be obtained by allowing it to pass into bottles containing water. We may regard the molecule of hydrogen sulfate as losing oxygen to form sulfurous acid, and the copper as forming copper oxide, which dissolves in acid to form copper sulfate:



(Write the equation by the electron method.)

The action of concentrated sulfuric acid upon copper is complicated, considerable quantities of copper sulfide (black) also being produced.

In the case of carbon and sulfur, respectively, the chemical changes are as follows:



(IV) **By treating sulfites with acids.** Sulfur dioxide may be very conveniently prepared by treating a sulfite with an acid. Sulfurous acid is first formed, which dissociates into sulfur dioxide and water:



This method is analogous to the preparation of carbon dioxide by treating a carbonate with an acid, and it is a convenient one for the laboratory.

334. Physical Properties. — Sulfur dioxide is a colorless gas possessing the sharp, suffocating odor of burning sulfur. Its specific gravity (air = 1) is 2.264. The gas may be readily liquefied at atmospheric pressure by passing it through a vessel surrounded by ice and salt in the ratio of 3 : 1 (Fig. 119). The colorless liquid boils at -8° , and freezes to a white solid which melts at -76° . The C.T. of the gas is 157° and the C.P. 77.65 atmos. Liquid sulfur dioxide for industrial purposes is stored in metal cylinders. Sulfur dioxide is quite soluble in water, 1 vol. of the liquid at S.T.P. dissolving 80 vols. of the gas, forming sulfurous acid. On exposing the solution to the air

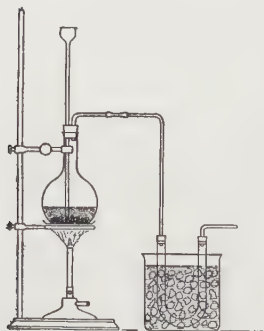
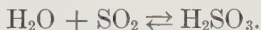


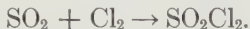
FIG. 119.

much of the gas escapes, and it may be completely expelled by boiling.

335. Chemical Properties. — Sulfur dioxide combines with water to form *sulfurous acid*:



The gas unites directly with chlorine in sunlight to form **sulfuryl chloride** (SO_2Cl_2), a fuming liquid:



In SO_2 , sulfur has a valence of 4, while in SO_2Cl_2 and SO_3 it has a valence of 6. SO_2 is an unsaturated compound, for it has a tendency to combine with such elements as chlorine and oxygen to form compounds in which sulfur has a valence of 6. SO_2 is, therefore, a good reducing agent.

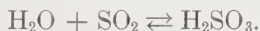
Sulfur dioxide bleaches many materials, such as straw, paper,

silk, and wool. It is much milder in its action than chlorine, which would injure silks, woolens, etc. The bleaching action of sulfur dioxide may be shown by introducing a colored flower, thoroughly moistened with water, into a bell-jar containing sulfur dioxide, or sulfur burning in oxygen. In bleaching, water is necessary, and it is likely that sulfurous acid forms unstable compounds with the organic coloring matter. A red rose bleached in an atmosphere of sulfur dioxide may have its color restored by dipping it into moderately concentrated nitric acid.

336. Uses of Sulfur Dioxide. — Immense quantities of sulfur dioxides are used in the manufacture of sulfuric acid and sulfites. Large quantities also are used in bleaching. It also is used to some extent as a refrigerant and as a preservative and disinfectant, but formaldehyde has largely displaced it for the latter purpose.

SULFUROUS ACID, H_2SO_3

337. Preparation and Properties. — Sulfurous acid is prepared by dissolving sulfur dioxide in water:

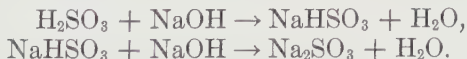


As the acid is very unstable, it is known only in solution. When SO_2 is led into water, only a portion of the substance combines with water, the other portion being dissolved physically. All the SO_2 may be expelled by heating the solution. Sulfurous acid is a weak dibasic acid:



In dilute solution, a little $\text{SO}_3^{=}$ is formed.

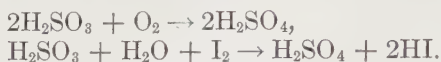
Sulfurous acid forms two salts with each metal or base, namely, **bisulfites** and **sulfites**. The formation of the sulfites of sodium may be represented thus:



(What action will solutions of these salts have upon litmus? Explain.)

NaHSO_3 is used as an antichlor, *i.e.*, for removing excess of chlorine from materials bleached by the action of the latter. *Calcium bisulfite*, $\text{Ca}(\text{HSO}_3)_2$, is used on a very large scale in the manufacture of paper on account of its ability to dissolve lignin, the substance that cements the fibers of cellulose in wood.

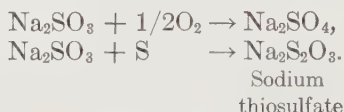
Sulfurous acid is a good reducing agent, for it has a tendency to take up oxygen to form H_2SO_4 :



In this respect sulfurous acid is similar to its anhydride.

When sulfurous acid is exposed to the air or oxygen, it is gradually oxidized to sulfuric acid. This may be proved by acidifying the solution with hydrochloric acid and then adding barium chloride. BaSO_4 is practically insoluble in hydrochloric acid, while BaSO_3 is soluble.

Sulfites combine with oxygen to form sulfates, and with sulfur to form thiosulfates:



SULFUR TRIOXIDE, SO_3

338. Preparation. — Sulfur trioxide (sulfuric anhydride) is manufactured on a large scale by passing a mixture of sulfur dioxide and oxygen over heated platinized asbestos or platinized magnesium sulfate:



This action is both reversible and exothermic. To increase the yield of SO_3 a large excess of oxygen must be employed and too high a temperature must be avoided.

With spongy platinum as catalyst the reaction may be carried out at 400 – 450° ; but with less active catalysts the temperature is higher (500° , or more). "Asbestos contact mass" containing about 10 per cent of platinum and "magnesium sulfate contact mass" containing 0.25 per cent of the metal are very effective accelerators. The latter is known as the Grillo contact material. When silica gel (474) is employed as a base, the amount of platinum may be still further reduced. When these are employed as catalysts, the temperature is approximately 450° , and about 95 per cent of the gases unite. Other catalysts, such as Fe_2O_3 (burnt pyrite) and Cr_2O_3 , may be used, but they are less active. Since the minutest quantities of arsenic, dust, etc., formed by roasting

the sulfide, "poison" the catalyst, the sulfur dioxide must be carefully purified.

Enormous quantities of SO_3 are used in the manufacture of sulfuric acid (343). The vapor is absorbed in concentrated sulfuric acid, in which it dissolves much better than in water.

The preparation of a small quantity of sulfur trioxide may be accomplished by allowing dry SO_2 and O_2 to pass through a hard-glass tube containing platinized asbestos heated to about 400° . The fumes may be condensed in a U-tube surrounded by a freezing-mixture

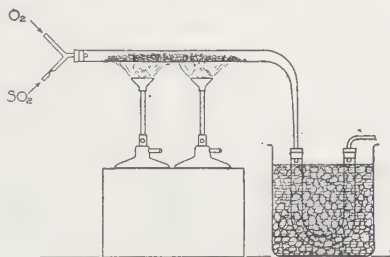


FIG. 120.

(Fig. 120). The oxygen and the sulfur dioxide are dried by means of concentrated sulfuric acid.

Sulfur trioxide also may be formed by heating certain bisulfates and sulfates:



Potassium Potassium
bisulfate pyrosulfate



Ferric
sulfate

339. Physical Properties. — Sulfur trioxide is a colorless liquid, which boils at 45° . The liquid solidifies to form crystals melting at about 17° . A polymeric modification may be obtained as white crystals resembling asbestos by allowing the liquid form to stand in the presence of a trace of moisture. When this form of the anhydride is heated to 50° , it passes into vapor (SO_3) without melting.

340. Chemical Properties. — When SO_3 is exposed to the air it fumes strongly, due to the formation of droplets of sulfuric acid:



When placed in water, it reacts vigorously to form sulfuric acid. The compound is therefore the anhydride of sulfuric acid, and is a powerful dehydrating agent. Sulfur trioxide also interacts energetically with certain metallic oxides to form sulfates:



Sulfur dioxide combines, with incandescence, with certain solid metallic peroxides to form sulfates:



Sulfur trioxide dissociates at high temperatures:



At 700°, the dissociation amounts to about 40 per cent. Sulfur trioxide unites with H_2SO_4 to form *pyrosulfuric acid*:



SULFURIC ACID, H_2SO_4

341. History. — Sulfuric acid was obtained in the fifteenth century by heating green vitriol ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) with sand; hence the name "oil of vitriol," or "vitriolic acid." The acid thus prepared was very crude. About the middle of the eighteenth century, Ward, a quack doctor of England, manufactured sulfuric acid by burning a mixture of sulfur and saltpeter in ladles suspended in glass globes containing small quantities of water. The capacity of the globes was from 40 to 50 gallons. The acid was crude and expensive, selling for 13 shillings (\$3.25) per pound. Leaden chambers were soon substituted for the glass globes, which was a great step in advance. Such chambers were first constructed in Birmingham in 1746.

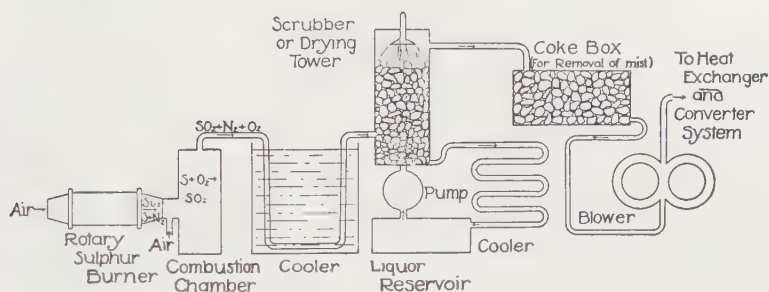
It is interesting to know that Squire and Messel in England and Winkler in Germany almost simultaneously (1875) took out patents for the manufacture of fuming sulfuric acid by "contact" processes. It was largely owing to the labors of Knietseh and Krauss (1901) that the commercial manufacture of sulfuric acid by the contact process was made a great success.

342. Manufacture. — There are two processes employed in the manufacture of sulfuric acid — the Contact Process and the Lead-Chamber Process. Both processes are employed on a large scale. For producing very pure, concentrated sulfuric acid, the contact process is superior; but for the production of dilute acid, pure enough for the manufacture of fertilizer (superphosphate of lime) and for certain other purposes, the chamber process is cheaper and is still extensively employed.

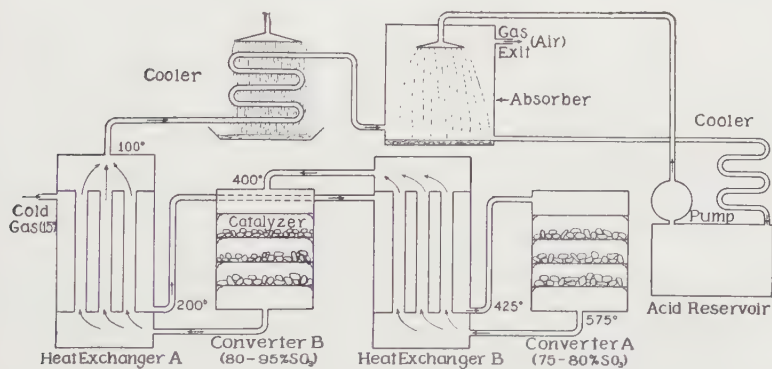
343. The Contact Process. — Sulfuric acid is produced on a large scale by allowing sulfur trioxide to interact with water:



Sulfur dioxide is first prepared by burning sulfur or by roasting a sulfide in air. Iron pyrites, FeS_2 , is used for this purpose; but in recent years the demand for pyrite has decreased, as sulfur has largely displaced it in the manufacture of sulfuric acid. We have already seen under what conditions sulfur dioxide and oxygen (from the air) unite to form sulfur trioxide. Some of the conditions for making this process a success are as follows: (1) the sulfur



I. Gas Preparation and Precipitation System.



II. Heat Exchanger, Converter, and Absorption System

FIG. 121.

dioxide must be free from particles of dust, arsenic trioxide, etc., which "poison" the catalyst and inhibit its action; (2) the temperature must be maintained approximately at 470° ; (3) twice the quantity of oxygen demanded by theory is employed; (4) as sulfur trioxide vapor is not dissolved readily by water, the gas is

passed into sulfuric acid 97 to 99 per cent in strength. The concentration of the absorbing acid is kept constant by running in water as the trioxide is taken up.

All concentrations of acid, and even pyrosulfuric acid, can be produced in the same works, and no costly lead chambers and niter are required.

The manufacture of fuming sulfuric acid or "oleum" (a solution of SO_3 in concentrated sulfuric acid) is shown by means of the accompanying diagram (Fig. 121). Sulfur is burned in a Rotary Sulfur Burner, from which the gases pass to the Combustion Chamber to complete the combustion of sulfur to SO_2 . After leaving the Cooler the gases pass through the Scrubber, or Drying Tower, where they are washed with sulfuric acid; thence through the Coke Box for the removal of mist. By means of a Blower the gases are next sent through Heat Exchangers *A* and *B* in order to raise the temperature to about 425° . They now enter Converter *A*, where, in the presence of the catalyst spread upon trays¹ (Grillo Process), the conversion of SO_2 to SO_3 is 75 to 80 per cent, the temperature rising to about 575° . The hot gases now pass through Heat Exchanger *B*, the temperature falling to about 400° . In passing through Converter *B* the percentage of SO_3 may rise to 95. The gases are now cooled down in preparation for the absorption of SO_3 , by passing them through Heat Exchanger *A* and the Cooler. Finally, the gases are sent to the Absorber where the SO_3 is absorbed in concentrated sulfuric acid, forming "oleum." The residual gases (N_2 , O_2 , etc.) escape into the air and the acid collects in the Acid Reservoir.

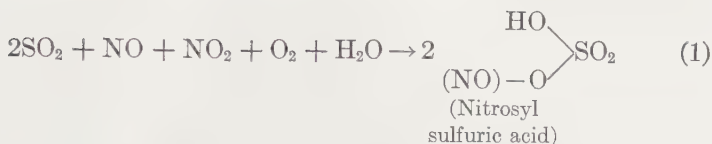
344. The Lead-Chamber Process. — The following gases are brought together in large leaden chambers:

- (1) Sulfur dioxide, obtained by roasting metallic sulfides or by burning sulfur.
- (2) Oxides of nitrogen ($\text{N}_2\text{O}_3 \rightleftharpoons \text{NO} + \text{NO}_2$) from nitric acid.
- (3) Oxygen from the air.
- (4) Steam, or atomized water.

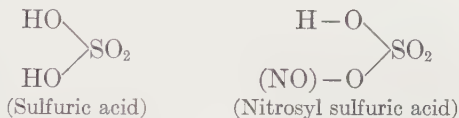
Since all the interacting substances are gaseous and the reactions are not speedy, large chambers are required.

Chemists are not in full agreement as to all the chemical changes which occur in the chambers, but according to Lunge they are as follows:

¹ The contact mass is generally employed in tubular converters and not on trays.

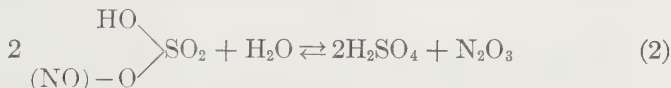


Nitrosyl sulfuric acid may be regarded as a derivative of sulfuric acid, in which one atom of hydrogen has been replaced by the nitrosyl group (NO):



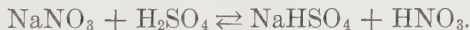
By limiting the quantity of steam admitted to the chambers, nitrosyl sulfuric acid may form white crystals known as "chamber crystals."

The nitrosyl sulfuric acid interacts with water as follows:



As N_2O_3 is unstable, it dissociates into NO and NO_2 .

The oxides of nitrogen are absorbed in concentrated sulfuric acid, and dilute sulfuric acid collects upon the floors of the chambers. There is some loss of the oxides of nitrogen, so the supply may be kept up by allowing sodium nitrate and sulfuric acid to interact:



Oxides of nitrogen are formed, due to the reducing action of SO_2 upon HNO_3 :



The chief parts of a sulfuric acid plant (Fig. 122) are as follows:

(1) **Furnaces for producing SO_2** (pyrites-kilns, or burners, *B*). In one or more of the burners a "niter pot," *N*, may be set to supply nitrous gases; or, the pots may be placed in a small chamber built into the flue. SO_2 also is produced by burning sulfur in rotary burners, since sulfur is displacing pyrites in the production of sulfuric acid.

(2) **The Glover Tower.** This is placed next to the burners; its functions are several, one of which is to liberate the nitrogen oxides from nitrosyl sulfuric acid obtained in a later stage of the operation. It is termed the denitrating tower.

(3) **The Lead Chambers.** There are usually from 3 to 5, with a total capacity of 140,000 to 200,000 cu. ft. As a rule, the

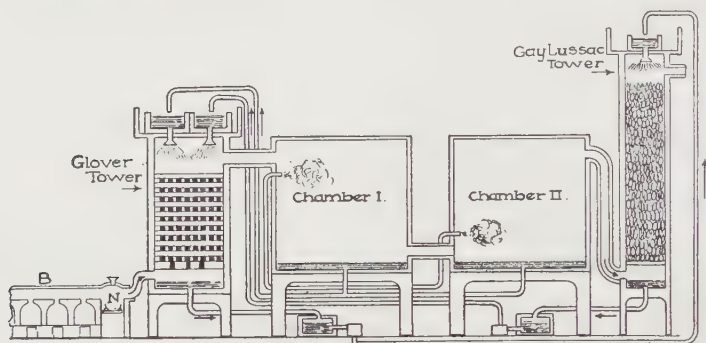


FIG. 122.

first chamber is the largest, and the greater part of the acid is formed in it.

(4) **The Gay-Lussac Tower.** The function of this tower is the recovery of the oxides of nitrogen by dissolving them in concentrated sulfuric acid.

(5) **The Concentrating Apparatus.**

Following are some of the details connected with the production of sulfuric acid:

Sulfur dioxide and the necessary amount of air pass into the Glover tower where they are impregnated with oxides of nitrogen. From the Glover tower the gases pass into the leaden chambers into which water or steam is injected. The gases interact to form sulfuric acid, which collects in the chambers until it contains from 60 to 70 per cent of H_2SO_4 . The oxides of nitrogen pass into the Gay-Lussac tower where they are absorbed by moderately concentrated sulfuric acid which trickles down over layers of tile or coke. This acid is pumped up to the top of the Gay-Lussac tower from the bottom of the Glover tower, and its sp. gr. is about 1.75. Acid of this concentration absorbs oxides of nitrogen. The solution of oxides of nitrogen in sulfuric acid ("nitrous vitriol") is run into the top of the Glover tower, where it is diluted with "chamber acid" or water until its sp. gr. is about 1.6. This acid passes down the tower and comes in contact with hot sulfur dioxide and steam, and oxides of nitrogen are liberated. This process is repeated over and over. As the lower part of the Glover tower is hot, considerable water is lost by evaporation, and the acid becomes sufficiently concentrated to use in the Gay-Lussac tower for absorbing oxides of nitrogen.

The chamber acid, which as a sp. gr. of 1.53 to 1.62 (60 to 70 per cent of H_2SO_4), is concentrated by first evaporating it in shallow leaden pans until the sp. gr. is 1.70. When the sp. gr. of the acid is above 1.70, it attacks lead, so the more concentrated acid must be obtained by employing vessels which are not appreciably attacked by the acid, such as silica or silico-iron.

One process employed is known as the **cascade system**. Basins are placed over an inclined flue which is fired at the lower end. Dilute sulfuric acid is delivered continuously to the basin at the top, from which it flows by a spout to the vessel below, etc. The acid becomes more and more concentrated as it flows from basin to basin, for the temperature increases.

Concentrated acid may be conveniently obtained by mixing the dilute acid with "oleum." The ordinary concentrated sulfuric acid of commerce usually contains about 95 per cent of H_2SO_4 and its sp. gr. is about 1.84. The most concentrated acid obtainable by distillation contains about 98 per cent of H_2SO_4 and 2 per cent of water.

Commercial sulfuric acid prepared by the chamber process is never pure; it always contains water and in addition such impurities as lead sulfate, as well as arsenic derived from the sulfides. Pure sulfuric acid may be prepared by distilling the commercial acid from vessels made of glass, porcelain, or silica.

345. Physical Properties. — Sulfuric acid obtained by distillation is a heavy, oily liquid sometimes called "oil of vitriol." If the distillate containing about 98 per cent of H_2SO_4 be cooled considerably below 0° , white crystals of hydrogen sulfate are formed, which melt at 10.5° . The sp. gr. of the liquid at 15° is 1.837. When the pure acid is heated, it fumes, by reason of partial dissociation into water and sulfur trioxide. The latter escapes until the acid contains 98.33 per cent of H_2SO_4 . The liquid then boils constantly at 338° without change in concentration. Sulfuric acid dissolves in water with considerable evolution of heat. *Always pour sulfuric acid into water rather than water into sulfuric acid.* When the acid is poured into water, it mixes quietly with the latter.

346. Chemical Properties of Hydrogen Sulfate. — Hydrogen sulfate is only moderately stable. When heated above 100° , its dissociation into water and sulfur trioxide is marked:



At 450° the dissociation is complete. When concentrated sulfuric

acid is dropped into red-hot iron retorts, it yields SO_2 and O_2 :



Concentrated sulfuric acid is an oxidizing agent. This is due to the tendency of the molecule to give up an atom of oxygen to form sulfurous acid:



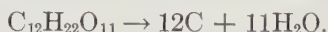
Sulfur trioxide dissolves in hydrogen sulfate to form pyrosulfuric acid (oleum):



Most of the metals interact with hydrogen sulfate, especially when they are heated together. Thus, we have seen that copper forms sulfur dioxide (333). Platinum and gold are appreciably attacked by the hot acid. Concentrated sulfuric acid and such metals as zinc and magnesium do not interact to form hydrogen, for hydrogen-ion is not present.

In general, hydrogen sulfate decomposes salts of other acids having boiling points lower than that of sulfuric acid. The preparation of hydrochloric acid (271) is a typical example. On account of its high boiling point, stability, and cheapness, sulfuric acid is the most important acid used in the preparation of other acids.

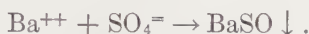
Hydrogen sulfate interacts vigorously with water to form one or more hydrates. Thus, $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ is a fairly stable compound. Concentrated sulfuric acid has, therefore, great affinity for water: *e.g.*, it abstracts the elements of water from many organic compounds, such as sugar ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) and starch ($\text{C}_6\text{H}_{10}\text{O}_5$)_x. This may be shown very impressively by pouring the acid into a very concentrated solution of cane sugar. Much heat is evolved, the sugar being converted largely into carbon and water:



Wood, paper, and cotton are also charred by sulfuric acid.

347. Chemical Properties of Sulfuric Acid. — Aqueous solutions of hydrogen sulfate have properties quite different from those discussed in the previous section; for in the case of dilute solutions the actions are ionic, while in that of hydrogen sulfate they are molecular. Sulfuric acid is an active, dibasic acid. The components of the solution are: H_2SO_4 , H^+ , HSO_4^- , and $\text{SO}_4^{=}$, the concentration of the last increasing with dilution. Sulfate-ion

($\text{SO}_4^{=}$) unites with barium-ion (Ba^{++}) to form barium sulfate, a white precipitate which is very insoluble in water and in dilute acids:



An acid solution of barium chloride is used in testing for sulfuric acid and soluble sulfates (or sulfate-ion).

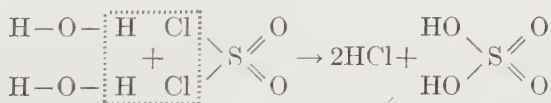
Dilute sulfuric acid interacts with the more active metals to form hydrogen and sulfates.

Sulfates. Sulfuric acid and bases interact to form acid sulfates, or bisulfates, and normal (neutral) sulfates: *e.g.*, sodium bisulfate, NaHSO_4 , and sodium sulfate, Na_2SO_4 . Certain sulfates are known as **vitriols**:

Blue vitriol.....	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
Green vitriol.....	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
White vitriol.....	$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$

Epsom salt, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$; *gypsum*, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$; and *potash alum*, $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$, are other important sulfates.

348. Constitution of Hydrogen Sulfate.—Sulfuric acid is formed when sulfuryl chloride SO_2Cl_2 is treated with water. This reaction indicates that H_2SO_4 contains two hydroxyl groups which are in union with the atom of sulfur:



The formula of hydrogen sulfate is often written $\text{SO}_2(\text{OH})_2$. Moreover, the acid forms two salts with each metal or base.

349. Uses.—Sulfuric acid is the most important and useful acid known. Next to water, it is the fluid most widely employed in the chemical industries, and is appropriately called the “vital fluid of the nation’s industries.” The acid plays such an important part in industrial chemistry that it has been said that a country’s prosperity and civilization may be estimated roughly from its output of sulfuric acid. Without this acid, commerce, manufacturing, transportation, as well as many affairs in the home, would be paralyzed. There is scarcely an article of clothing or a household utensil or fixture which is not dependent either directly or indirectly upon sulfuric acid. It is employed in almost every art and trade. Thus, it is utilized in the production of other acids,

such as nitric and hydrochloric; it also is employed extensively in petroleum refining, in metallurgy, and in the manufacture of steel, leather, alums, and blue vitriol.

Deprived of this acid, we could not operate our lead storage-batteries, manufacture explosives, or transform insoluble phosphate rock or bone-ash into soluble acid phosphate, so necessary in agriculture. Through the agency of sulfuric acid, starch is transformed into glucose, and copper is refined by electrolysis. Immense quantities of the acid are combined with ammonia to form *ammonium sulfate*, one of the most important fertilizers. The world's output of sulfuric acid in 1907 was about 4,000,000 tons; but just before the war the production was about 8,000,000 tons, over one-fourth of which was manufactured in the United States. According to A. E. Wells of the Bureau of Mines, our total manufacturing capacity on November 1, 1918, was 6,000,000 tons per year (basis 100 per cent H_2SO_4). Of this total capacity 40 per cent was at contact acid plants.

The domestic production of sulfuric acid in 1920 was valued at about \$70,000,000. New Jersey, Pennsylvania, Maryland, Illinois, Tennessee, Ohio, and Georgia were the largest producers; but it was produced in over 200 plants in 32 states.

OTHER OXYGEN ACIDS OF SULFUR

350. Pyrosulfuric Acid. — We have seen that sulfur trioxide and sulfuric acid interact to form pyrosulfuric acid, $\text{H}_2\text{S}_2\text{O}_7$ (340). This is a solid compound. "**Oleum**" is hydrogen sulfate containing about 20 per cent of pyrosulfuric acid; it is used extensively in chemical industries. The acid fumes when exposed to air. The old "Nordhausen" or "fuming" sulfuric acid contained from 10 to 20 per cent extra of SO_3 . The salts of pyrosulfuric acid are called **pyrosulfates** (Greek, meaning *fire*); they may be obtained by heating acid sulfates:



The bisulfates of sodium and potassium are often employed as *fluxes*. For instance, in analytical operations silica (SiO_2) may be separated from alumina (Al_2O_3) and ferric oxide (Fe_2O_3) by fusing the mixture in a platinum crucible with the bisulfate. Silica is not attacked, but alumina and ferric oxide are transformed into soluble sulfates. It is of interest to note, also, that alumina and ferric oxide can be separated from silica by adding hydrofluoric

acid and then evaporating to dryness; SiO_2 is transformed into SiF_4 , which is gaseous (302).

351. **Thiosulfuric Acid.** — *Thiosulfuric acid*, $\text{H}_2\text{S}_2\text{O}_3$, is unknown in the free state. *Sodium thiosulfate*, its most important salt, may be prepared by boiling a solution of sodium sulfite with sulfur:



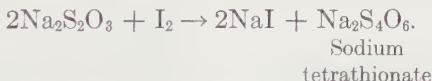
This action is similar to the addition of oxygen to sulfurous acid. The hydrate, $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, is commonly known as “**hypo**,” and its solution is used in photography in the fixing bath as a solvent for silver salts.

When a solution of sodium thiosulfate is treated with an acid, sulfur and sulfur dioxide are set free:



The sulfur which is deposited is yellow.

An iodine solution is decolorized by a solution of a thiosulfate:



(Explain this action according to the ionic theory.)

352. **Persulfuric Acid.** — This acid, which has the formula $\text{H}_2\text{S}_2\text{O}_8$, can be formed at the anode by the electrolysis of fairly concentrated sulfuric acid in which the ion HSO_4^- predominates:



The anhydride of persulfuric acid is S_2O_7 , a liquid:

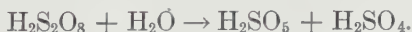


Sulfur heptoxide may be obtained by subjecting a mixture of dry sulfur trioxide and oxygen to the silent electric discharge (see Ozone).

Permonosulfuric acid (*Caro's acid*) is formed when sulfur trioxide is treated with hydrogen peroxide:

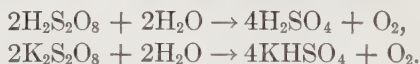


Dilute solutions of persulfuric acid are fairly stable, but gradually interact with water:

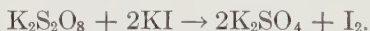


True per-acids are formed, as a rule, by the action of hydrogen peroxide upon an ordinary acid. Per-acids give rise to hydrogen peroxide on treatment with dilute sulfuric acid. This applies to their salts as well as to the free acids. Per-acids may be regarded as derivatives, therefore, of hydrogen peroxide. The elements which form per-acids belong to Groups III, IV, V, and VI of the Periodic System. Such acids as perchloric (HClO_4) and permanganic (HMnO_4) do not answer to the above definition, and are not regarded as true per-acids.

Persulfates, or the salts of persulfuric acid, are powerful oxidizing agents, and find application as such. Ammonium persulfate, a white crystalline compound, may be prepared by electrolysis, a saturated solution of ammonium sulfate being employed at the anode and fairly strong sulfuric acid at the cathode. The salt is collected in a porous pot. In a similar manner, potassium persulfate is produced by electrolysis, a solution of KHSO_4 being employed at the anode. *The persulfates are soluble in water, and are gradually decomposed by it, oxygen being formed:*

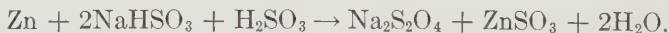


Persulfates liberate the halogens from halides:

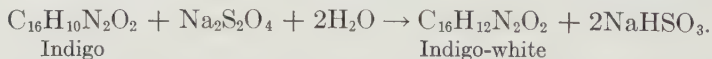


Persulfates were first prepared by Hugh Marshall (1891).

353. Other Oxyacids of Sulfur. — **Sodium hyposulfite**, a salt of hyposulfurous acid ($\text{H}_2\text{S}_2\text{O}_4$) is used by the calico printer and dyer as a reducing agent for indigo. A solution of the salt may be obtained by the interaction of zinc, sodium bisulfite, and sulfurous acid:



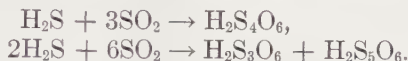
Indigo, an insoluble compound, is reduced by sodium hyposulfite to indigo-white, which is soluble:



When cloth is treated with the mixture, and then exposed to the air, oxygen is taken up and indigo re-formed.

The **polythionic acids** (di-, tri-, tetra-, penta-, and hexathionic

acids) are not of great importance. They may be formed, along with free sulfur, by passing SO_2 and H_2S alternately into *water*:



We have seen that sodium tetrathionate ($\text{Na}_2\text{S}_4\text{O}_6$) is formed when sodium thiosulfate is treated with iodine (351). (What change occurs when the *gases* SO_2 and H_2S interact?)

EXERCISES

1. Write the names and formulae of four oxides of sulfur, and equations to show that they are acid anhydrides.

2. Write names and formulae of the most important oxyacids of sulfur.

3. Give the occurrence, preparation (laboratory and industrial), physical properties, chemical properties, and the uses of sulfur dioxide. Why is it regarded as an unsaturated compound?

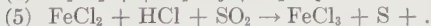
4. Write chemical equation to show the action of strong sulfuric acid upon mercury.

5. When strong sulfuric acid acts upon copper, copper sulfide is formed as well as copper sulfate. Explain.

6. Give several uses of sulfur dioxide, stating any principles upon which its uses are based.

7. Show that sulfur dioxide may function as an oxidizing agent as well as a reducing agent.

8. Complete the following equations:



9. How is sulfurous acid prepared? What are its properties, and how does it ionize in water? How would you prepare NaHSO_3 and Na_2SO_3 ? For what are sulfurous acid and sulfites used?

10. Outline the contact method for the manufacture of sulfur trioxide and sulfuric acid. Under what conditions are the best yields obtained? What are the most effective catalysts? What are the physical and chemical properties of SO_3 ?

11. Describe as fully as you can the lead-chamber process for the manufacture of sulfuric acid, writing the chemical equations involved. What advantages, if any, has this method over the contact process? How is the "chamber acid" concentrated and purified? Explain why lead sulfate and arsenic may occur as impurities in commercial sulfuric acid.

12. What are the physical properties of concentrated sulfuric acid? Tell how you would prepare an acid containing about 98 per cent of H_2SO_4 ; also pure hydrogen sulfate.

13. Give six chemical properties of concentrated sulfuric acid and illustrate as fully as you can by means of equations.

14. What are the chemical properties of dilute sulfuric acid? Give a good chemical test for it. Write chemical equations to show the action of both dilute and concentrated sulfuric acid upon zinc.

15. Why is concentrated sulfuric acid often called "oil of vitriol"? Write names and formulae of some very important sulfates. Write chemical equations showing how they may be formed.

16. Enumerate several important uses of both concentrated and dilute sulfuric acid.

17. Why is the formula of sulfuric acid often written $\text{SO}_2(\text{OH})_2$? State all that this formula implies.

18. How would you prepare the following compounds: (1) pyrosulfuric acid; (2) sodium thiosulfate; (3) persulfuric acid; (4) potassium pyrosulfate; and (5) sodium bisulfate? Explain the action of a solution of sodium bisulfate upon litmus.

19. Explain the use of sodium thiosulfate ("hypo") in photography. How does it differ from sodium hyposulfite? Explain the use of the latter in dyeing.

20. (a) What are the polythionic acids, and how may they be formed?

(b) 40 cc. of a molar solution of sodium thiosulfate were required to decolorize 25 cc. of a solution of iodine. Find the normality of the iodine solution.

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CHAPTER XX

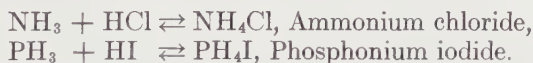
NITROGEN AND THE ATMOSPHERE. THE HELIUM GROUP

NITROGEN. N = 14.01

354. **Relationships and General Characteristics.** — Nitrogen is a member of Group V of the Periodic System, and is closely related to phosphorus; it is also related to the Arsenic Group; but as arsenic, antimony, and bismuth are classed with the metals in our scheme of chemical analysis, they will be studied in detail in a subsequent chapter (XXXV).

Nitrogen is a colorless gas, while phosphorus is a solid. Nitrogen and phosphorus are strictly acidic in character, but the acids of nitrogen (see Nitric Acid) are stronger than those of phosphorus. They form analogous oxides (N_2O_3 , N_2O_5 , P_2O_3 , P_2O_5).

Nitrogen and phosphorus form similar gaseous hydrides, namely, ammonia (NH_3) and phosphine (PH_3), both of which possess basic properties, *i.e.*, unite with acids to form salts:



The two elements also form analogous chlorides (NCl_3 , PCl_3), but nitrogen trichloride is one of the most unstable compounds known.

Nitrogen and phosphorus form similar metallic binary compounds: *e.g.*, magnesium nitride (Mg_3N_2) and calcium phosphide (Ca_3P_2).

In Chapter XXXV all the elements of Group V will be compared and contrasted.

355. **Importance and Occurrence.** — Nitrogen is an indispensable element, for all life is dependent upon it. While this is true, it also is a fact that neither animals nor plants, with the exception of certain families of micro-organisms, possess the faculty of taking nitrogen directly from the air, of which it constitutes about four-fifths by volume. While nitrogen does not appear to play an active rôle in the air as does oxygen, it is essential; for animal life in an atmosphere of pure oxygen would soon pass into an abnormal state and die.

Nitrogen occurs in the air in the free state and in enormous quantity. There are about 20,000,000 tons of nitrogen above each square mile of the earth's surface. Since there are 640 acres in a square mile, a farmer owning this amount of land may lay claim to nitrogen enough to supply necessary nitrogen compounds to the whole world for fifty years at the present rate of consumption. From 20,000,000 tons of nitrogen, 120,000,000 tons of pure Chile saltpeter, or sodium nitrate, could be produced.

The greater abundance of free nitrogen is due to its inertness under ordinary conditions and to the further fact that many nitrogen compounds are more or less unstable and therefore tend to give up nitrogen to the atmosphere. Moreover, nitrates, ammonia, and certain other nitrogen compounds are soluble in water and do not therefore enter into the composition of the outer crust of the earth as do many compounds containing such elements as oxygen, silicon, calcium, aluminium, and iron. Clay, or aluminium silicate, for instance, is insoluble and very abundant.

Nature cannot construct a cell without nitrogen. The marvellous properties of all living matter depend in part upon the presence of the element. Furthermore, it is an essential constituent of all commercial explosives, such as guncotton and trinitroluene (TNT), as well as of valuable fertilizers, such as Chile saltpeter and ammonium sulfate; also of nitric acid, ammonia, certain useful drugs, medicines, and dyes. Despite its apparent inertness and lack of odor, color, or taste, all life would sicken and die if deprived of nitrogen or of nitrogenous compounds. Bountiful harvests and vigorous growth of grass, flowers, and trees are dependent upon proper nitrogenous fertilizers.

Arrhenius has estimated that 400,000,000 tons of fixed nitrogen fall annually into the earth and sea as the result of electrical action. Nitrogen thus fixed is a valuable source of nitrogenous food for growing plants. The fixation of atmospheric nitrogen is of vast economic importance, owing to its use in the production of fertilizers and explosives, which are needed in time of peace as well as in war. Chile saltpeter (NaNO_3) is one of the most important sources of nitrogen.

356. History and Preparation. — Dr. D. Rutherford, Professor of Botany in the University of Edinburgh, recognized nitrogen as a distinct substance in the year 1772. He introduced animals into closed vessels, and then absorbed the carbon dioxide ("fixed air") in caustic potash. The residual gas failed to support the life of animals and it extinguished a burning candle. Nitrogen

was first found to be a simple substance by Lavoisier, who named it *azote*, the name still used by the French. Chaptal (1823) suggested the name **nitrogen** (Greek, *saltpeter* + *to produce*), because it is a constituent of saltpeter.

Nitrogen may be obtained from the atmosphere or from certain nitrogen compounds.

(I) **From the Atmosphere.** Nitrogen may be prepared by removing the oxygen of the air. This is accomplished by passing air over hot copper. Cupric oxide is formed which may be reduced by hydrogen or natural gas, and then used again. Nitrogen thus prepared is not pure, for it contains argon and smaller amounts of other gases. Phosphorus also may be used to remove oxygen from the air. Commercially, the chief source of nitrogen is liquid air. The liquid is allowed to evaporate and the more volatile nitrogen passes off first, leaving oxygen behind. Both products are valuable.

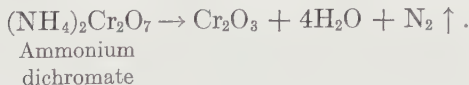
(II) **Laboratory Method.** Nitrogen may be readily prepared by heating *ammonium nitrite* (NH_4NO_2):



Since this salt is both expensive and unstable, nitrogen is usually prepared in the laboratory by heating together sodium nitrite and ammonium chloride or ammonium sulfate. Ammonium nitrite is formed and then decomposes into water and nitrogen:



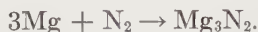
Nitrogen also may be prepared by heating *ammonium dichromate*, or a mixture of ammonium chloride and potassium dichromate:



Nitrogen may be collected either over water or mercury.

357. Physical Properties. — Nitrogen is a colorless, tasteless, odorless gas, which is only slightly soluble in water. It may be converted into a colorless liquid and a white solid. The C.T. is -147° and the C.P. is 33.5 atmos. The liquid boils at -195.5° , and the solid melts at -210.5° . The sp. gr. of nitrogen (air = 1) is 0.96717, and the weight of 1 liter is 1.2507 g. (Leduc).

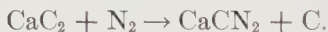
358. **Chemical Properties.** — Under ordinary conditions nitrogen is quite inactive; hence it occurs so abundantly in the free state. At high temperatures it combines directly with oxygen to form nitric oxide (NO), and with certain elements to form *nitrides*, such as Mg_3N_2 , Li_3N , Ca_3N_2 , and BN:



Nitrides are a possible source of ammonia (375).

Nitrogen also unites with hydrogen, in the presence of certain catalysts, to form ammonia. *Leguminous plants* (peas, clover,

etc.) assimilate free atmospheric nitrogen. This is brought about by the action of certain bacteria which live in the nodules on the roots (Fig. 123). Nitrogen also combines with hot calcium carbide (CaC_2) to form calcium cyanamide (CaCN_2):



It appears that an active form of nitrogen (N_3) has been prepared (see Ozone).



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FIG. 123. Nodules on Bean Roots Containing Nitrogen-fixing Bacteria.

359. **The Nitrogen Cycle.** — Nitrogen, as already stated, is essential for the growth of the bodies of animals and plants. It is found in combination in all living matter, and the waste products of animals contain combined nitrogen: *e.g.*, urea, $(\text{NH}_2)_2\text{CO}$. Animals cannot assimilate free nitrogen, but they

obtain it from nitrogenous foods — vegetable or animal. Most plants secure the required nitrogen from fertilizers — ammonium nitrate, manure, etc. — supplied to the soil. Certain plants, however, particularly the leguminosae (peas, beans, clover, etc.), are able to assimilate free nitrogen. Symbiotic bacteria appear to live as guests in the nodules on the roots of these plants, and they are able to convert free atmospheric nitrogen into complex substances needed for the growth of the plants. This fact is of

very great importance in agriculture. Thus, when clover is plowed under, the soil is enriched.

Nitrogen undergoes a never-ceasing cycle of changes in nature. Starting with free atmospheric nitrogen, it may be fixed by electrical discharge or by symbiotic bacteria, and thus rendered available as plant food. Plants serve as food for animals; and when plants and animals die and decay, ammonia, nitrates, nitrogen, etc., are formed. The nitrogen compounds enrich the soil for living plants, and the free nitrogen returned to the air repeats the cycle over and over through countless ages. "There is no atom of nitrogen in the air that has not at some time or other in the course of its existence throbbled through the tissues of a living plant or animal, not once but many times."

THE ATMOSPHERE

360. The Atmosphere has Weight. — The word **atmosphere** (Greek, *vapor* + a *sphere*) refers to the great ocean of aeriform fluid surrounding the earth, and commonly called the air. The latter term was used by the older chemists in the same sense as we now employ the word gas. Thus, oxygen was called "fire-air" and "dephlogisticated air," and carbon dioxide, "fixed air."

We have seen that the atmosphere exerts pressure (44), the normal pressure being 1033.2 g. per sq. cm., or almost 15 pounds per sq. in. We have also seen that the pressure varies from time to time. That the air has weight, or exerts pressure, may be shown very strikingly by boiling a small amount of water in a "tin" can. When all the air has been expelled from the can, it is tightly stoppered and then immersed in cold water. The steam condenses, and the can then collapses, due to the pressure of the surrounding air.

361. Composition of the Atmosphere. — The atmosphere contains as normal components the following gases, which are mechanically mixed: *nitrogen, oxygen, argon and other gases of the helium group, water vapor, and carbon dioxide.* It also contains small quantities of ammonia, oxides of nitrogen, hydrogen, and a very small quantity of some oxidizing agent, possibly ozone or hydrogen peroxide. The air also contains dust and ammonium nitrate (from the interaction of ammonia and nitric acid). Then, too, the atmosphere may contain accidental components, such as sulfur dioxide and hydrogen sulfide.

362. Nitrogen, Oxygen, and Argon. — The atmosphere is composed primarily of nitrogen, oxygen, and argon, which are present in almost constant proportions. Taking into consideration only the argon, the composition of pure, dry air is, according to Leduc, as follows:

	<i>By Volume</i>	<i>By Weight</i>
Nitrogen.....	78.06	75.5
Oxygen.....	21.00	23.2
Argon.....	0.94	1.3

At Cleveland, Ohio, Morley found the mean value of the oxygen by volume to be 20.93, which is identical with the value found by Hempel at Dresden. Regnault obtained the value 20.96 at Paris.

The oxygen may be removed from the air by the means of white phosphorus, or by passing it over heated copper. The nitrogen may then be removed by passing the residual gas over heated magnesium. The argon, being inactive, is left.

363. Carbon Dioxide. — Carbon dioxide is found in all specimens of air, the main sources of the gas being the combustion of fuel, the decay of vegetable and animal matter, and the process of breathing. Pure country air contains about 3 vols. of carbon dioxide per 10,000 vols. of air; while in large cities where much coal is burned, the amount of the gas may rise to 6–7 vols. per 10,000 vols. Crowded audience rooms sometimes contain as high as 50 parts of carbon dioxide per 10,000 vols.

Carbon dioxide is readily taken up by a solution of barium hydroxide or calcium hydroxide (limewater). The white precipitate obtained is a carbonate:



The gas may also be removed from air by means of caustic potash or soda-lime.

Air containing more than 7 vols. of carbon dioxide per 10,000 vols. should not, as a rule, be breathed for a long period of time. The deleterious properties of such air are probably due to certain organic impurities other than carbon dioxide, which are thrown off from the body during respiration. The quantity of carbon dioxide present in the air of a room is a good test as to whether or not it is fit for respiration. Ventilation is very important.

Some one has estimated that there are 2,450,000,000,000 tons of carbon dioxide in the atmosphere. The world's yearly consumption of coal is about 1,300,000,000 tons, and this produces

about 3 times that weight of carbon dioxide; but large as this quantity is, it would increase the amount of carbon dioxide in the air by only one six-hundredth. As a matter of fact, the total amount of carbon dioxide in the atmosphere is relatively constant; for plants take up carbon from carbon dioxide, and return oxygen to the air, thus tending to maintain a balance between these two gases (764).

364. Water Vapor. — Aqueous vapor is a very necessary component of the atmosphere. The capacity of the air for water vapor increases with rise in temperature; therefore, when air is cooled, it may become saturated. *When air is saturated with water vapor, the humidity is 100 per cent.* The average humidity is about 66 per cent. Why is there so much discomfort on a hot, humid day? This is due to the combination of high temperature and excessive humidity, which retards evaporation of perspiration from the skin. Ventilation or fanning affords relief, for evaporation is hastened; and this not only uses up heat, but removes the stationary layer of air next the skin.

When the temperature of saturated air is lowered, the water vapor condenses in droplets as dew, fog, or clouds; or it may be precipitated in the form of rain, snow, or hail. More than 140,000 tons of rain would be deposited by cooling one cubic mile of saturated air from 35° to 0°.

It is a well-known fact that moist air is lighter than dry air. The barometric pressure is high during fair weather.

Experiments indicate that if it were not for dust particles in the air, there would be no occurrence of fog, clouds, and rain. The particles of dust appear to serve as nuclei round which droplets of water form. In a dustless atmosphere umbrellas and awnings would be of no service, for the moisture would not be precipitated as rain, but would gradually condense upon the surfaces of objects.

Air may be dried by drawing it through tubes containing a dehydrating agent, such as calcium chloride or phosphorus pentoxide.

365. Bacteriology of the Air. — It has been stated that the air contains dust. Some of the dust is organic, a part of which consists of microscopic organisms (spores of moulds and yeasts, bacteria, etc.). There are from 4 to 5 microbes, on an average, in one liter of air, while a pure unfiltered river water contains from 6,000 to 20,000 in one cc., and natural soil about 100,000 per cc. It should be noted that bacteria do not find their way into the air from a moist surface. When the soil is dry and wind

currents are strong, bacteria pass into the atmosphere. After a prolonged rain, the air contains but few bacteria. The spores of moulds are most abundant, however, during warm, damp weather. The most dangerous factor, hygienically, is probably dust to which bacteria cling. This is particularly true of dust of dwellings, which may carry infectious microbes, such as the *tubercle bacillus*. Most of the microbes of the air, however, are saprophytic, such as the organisms producing fermentation and putrefaction. Dust can be removed from air by drawing it through wide tubes packed with 12–15 inches of cotton.

366. The Atmosphere a Mixture. — The following proofs show that the air is a mixture:

(1) The composition of the air varies more or less from time to time, consequently its composition cannot be represented by means of a chemical formula. Every chemical compound, on the other hand, is definite in composition (see Law of Definite Proportions).

(2) The components of the air retain their own properties, and the properties of air are the mean of those of the components.

(3) The components of the air may be separated by mechanical means. Thus, when liquid air is allowed to evaporate, the more volatile nitrogen escapes first, leaving a residue richer and richer in oxygen.

(4) When nitrogen and oxygen are mixed together in the ratio in which they are found in the air, no chemical action occurs, but the mixture has the essential properties of ordinary air.

367. Liquefaction of Air. — Liquid air is now produced on a large scale by a method invented independently by Hampson and Linde. This method is based upon the fact that, *when a gas under high pressure is allowed to expand through a small orifice, some of the heat energy of the gas is used up in overcoming the cohesion of the molecules and in separating them farther apart.* The following is a brief outline of the Hampson process:

The air is first freed of carbon dioxide by means of lime, after which it is compressed to 200 atmospheres. The heat generated by the compression of the gas is now absorbed by allowing the compressed gas to flow through pipes cooled by running water. As a consequence of the compression, most of the water vapor of the air is condensed; but the last traces of water vapor and carbon dioxide are removed by the use of solid sodium hydroxide. The air is now allowed to pass to the liquefier, the essential part of which is two concentric metal pipes wound in the form of a spiral, and well protected by means of a non-conductor of heat (Fig. 124). The highly compressed air is pumped down the inner tube (C) and allowed to escape through a small

orifice in the bottom. The gas therefore expands and falls in temperature. The cold gas now passes up the outer tube (*D*), and is again compressed and pumped back through the inner tube. While the gas is passing upward it cools the compressed air passing down the inner tube. The cold compressed gas is again allowed to expand, and consequently becomes still colder. This process is repeated until the gas liquefies. The liquid air is withdrawn from time to time by means of a valve.

Liquid air is kept in Dewar flasks (Fig. 125), which may be loosely stoppered with cotton. These flasks consist of one glass flask surrounded by another, the space between their walls being evacuated. The inner wall of the outer flask may be silvered in order to reflect the radiant energy of surrounding bodies. This principle is applied in the manufacture of Thermos bottles or flasks.



FIG. 125.

Liquid air is a pale-blue mobile liquid, boiling at about -190° . It is used as a cooling agent, and with charcoal it forms a blasting explosive. Its chief use is in the preparation of oxygen, nitrogen, and argon. Ordinarily it contains about 50 per cent of oxygen, but the percentage rises, as the nitrogen evaporates more rapidly.

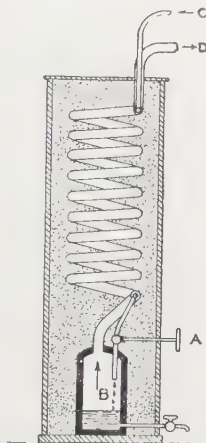


FIG. 124.

368. Experiments with Liquid Air. — (1) When liquid air is poured from a Dewar flask into a beaker, it boils freely.

(2) When such substances as rubber, eggs, beefsteak, and flowers are immersed in liquid air for a short while, they become very brittle. When a rubber ball, frozen in liquid air, is thrown against a hard object, it breaks like glass.

(3) A piece of glowing wood continues to burn when thrust into liquid air (Care! Thrust in one end of a glowing splinter).

(4) When liquid air is poured into a small teakettle placed upon a lump of ice, the liquid boils away.

(5) When a small "tin" can is partially filled with liquid air and then heated over a Bunsen burner, a coating of frost forms on the surface of the can.

(6) When alcohol or petroleum contained in a test-tube is immersed in liquid air, it freezes.

THE HELIUM FAMILY

369. Relationships and Properties. — The Helium Family contains the inert gases *helium*, *neon*, *argon*, *krypton*, *xenon*, and *radon*, which occupy Group 0 of the Periodic System. They are all

colorless, inert gases, and have, therefore, no active valence; that is, an atom of any of these elements has no valence electrons. This means that the outer orbit or sphere of the atom has eight planetary electrons. They are related in an interesting way to the Halogen and Alkali Families. To illustrate: The atomic numbers and weights of fluorine, neon, and sodium are respectively as follows (the numbers in parentheses are atomic numbers):

F (9)	Ne (10)	Na (11)
19	20.2	23

In passing from fluorine to neon there is an increase of one in the atomic number, and the same is true in passing from neon to sodium. It is assumed that the atom of the halogen element has seven valence electrons (valence + 7 or -1), while the atom of the alkali metal has one valence electron (valence + 1). When, therefore, an atom of a halogen gains an electron, it has eight outer electrons, or the outer orbit is full, as in the case of the atoms of the inert elements, which have a valence of zero. When an atom of an alkali metal combines with an atom of a halogen, we have already seen that the change may be regarded as a transfer of an electron from the metallic atom to the halogen atom, both atoms becoming ions.

Some of the facts concerning the elements of the Helium Family are summarized in the following table.

THE HELIUM FAMILY

Element	At. Wt.	At. No.	B.P.	M.P.	C.T.	C.P. (atmos.)	Parts in 1,000,000 Air
Helium, He....	4.00	2	-268.9°	-272.2°	-268.75°	2.75	4
Neon, Ne.....	20.2	10	-246°	-253°	-228.35°	26.8	10-20
Argon, A.....	39.94	18	-186°	-189.5°	-117.4°	52.9	9370
Krypton, Kr...	82.9	36	-152°	-169°	-62.5°	54.3	0.05
Xenon, Xe.....	130.2	54	-109°	-140°	+16.6°	58.2	0.006
Radon, Rn.....	222.0	86	-62°

370. **Argon, A.** — It was discovered by Lord Rayleigh, the English physicist, that a liter of nitrogen obtained from the air weighed 1.2572 g., while a liter of the gas prepared from different nitrogen compounds — ammonia, urea, etc. — had a mean weight of only 1.2505 g. The difference did not exceed one-half per cent, but it was much greater than the experimental error.

Lord Rayleigh adopted the hypothesis that the "atmospheric

nitrogen " is a mixture of chemical nitrogen and an unknown gas of greater density. In 1894, Rayleigh and Ramsay discovered argon in the atmosphere. Rayleigh repeated the experiments of Cavendish, and found that, after sparking oxygen and nitrogen and absorbing the products in an alkali, a residual gas was left. Ramsay passed atmospheric nitrogen over heated magnesium, which formed magnesium nitride (Mg_3N_2), leaving argon free.

It is of interest to know that Cavendish (1785) established the composition of nitric acid by passing electric sparks through a mixture of nitrogen and oxygen in the presence of moisture. After absorbing the products, together with the excess of oxygen, Cavendish concluded that the residual gas did not amount to more than 1/120th part of the whole.

Argon is a colorless, odorless, tasteless gas with the atomic weight of 39.94. It may be condensed to a colorless liquid which boils at -186.1° .

Argon (Greek, *idle, inactive*) has no active valence, for no compounds of the element are known. The molecule of argon is monatomic.

Argon is used for filling tungsten electric-light bulbs, for it produces greater brilliancy and prolongs the life of the bulbs.

371. **Helium, He.** — The element helium (Greek, *the sun*) was discovered in the sun through a spectroscopic observation (prominent orange line) made by the French astronomer Janssen during the solar eclipse on August 18, 1868, and the subsequent suggestions of the English scientists Lockyer and Frankland. In 1882 Palmieri observed the same orange line in the spectrum of the flaming gases of Vesuvius.

In 1895 Ramsay learned that Hillebrand, chemist of the United States Geological Survey, had obtained a gas from the mineral *uraninite*, which to the latter appeared to be nitrogen. Ramsay secured a specimen of uraninite (cleveite), heated it with sulfuric acid, collected the gas, and determined its spectrum, which was found to be identical with that of solar helium.

Helium is a colorless, odorless, tasteless gas with the atomic weight of 4. Like argon, it is monatomic. The spectrum of helium contains an orange line near the *D* line of sodium. Helium is the most difficult of the gases to liquefy. The boiling point of the liquid is about -269° .

Sir William Ramsay suggested the use of helium in air balloons. Its advantages are that it is incombustible and has about 92 per cent of the lifting power of hydrogen. The chief source of helium

is the gas fields of the Southwest. The Petrolia field of Texas yields about one per cent. The inflammable components of the gas are liquefied, leaving impure helium in the gaseous state. It is purified by passing it over activated charcoal at the temperature of liquid air, which results in the adsorption of all gases except helium and hydrogen. A few years ago helium cost about two thousand dollars a cubic foot, but now the price is only a few cents per cubic foot, which is, of course, much more expensive than hydrogen. There is apparently helium enough in sight to supply many airships of the size of the dirigible *Los Angeles*.

Helium also occurs in the air, there being about 1 volume in 250,000 volumes of air (Ramsay). It is produced by the spontaneous disintegration of radium. Except hydrogen, helium is the lightest gas known.

Helium is displacing nitrogen in synthetic air which is employed in deep-sea diving. Helium is less soluble in the blood than is nitrogen, and is therefore more rapidly eliminated when the diver comes to the surface.

372. Neon Ne, Krypton Kr, Xenon Xe. — Ramsay and Travers (1898) isolated the elements **neon** (Greek, *new*), **krypton** (Greek, *hidden*), and **xenon** (Greek, *stranger*) from crude argon prepared from the atmosphere. This was accomplished by liquefying the argon by means of liquid air, and then subjecting the clear liquid to fractional evaporation. Neon (B.P. -246°), accompanied by a certain proportion of helium, evaporated off first. Neon was then separated from helium (B.P. -268.9°) by the use of liquid hydrogen (B.P. -252.5°), which froze the neon and left the helium gaseous. Krypton and xenon were left in the end products of the distillation of the liquefied argon, and were separated by liquefaction and fractionation. Liquid krypton boils at -152° and xenon at -109° .

The molecules of the three new gases were found to be monatomic. Their atomic weights (see Isotopes), 20.2, 82.9, and 130.2 place them in Group 0 of the Periodic Table (Chap. V). They are chemically inactive.

According to Ramsay, there are about 1–2 parts of neon per 100,000 of air by volume, 1 part of krypton to 20,000,000, and 1 part of xenon to 170,000,000.

Certain tubes designed for illuminating purposes are filled with neon at low pressure, and a relatively small amount of electrical energy is required to make these tubes luminous; a red glow is produced.

As stated by D. H. Killeffer, powerful neon lights are coming rapidly into use as beacons for airplanes and ships to guide them through fogs and inclement weather. Their importance to safe navigation and to the development of air transport can hardly be overestimated. Beacons visible for fifty miles through a haze rendering lights of immense candlepower invisible within ten or twelve miles have been through the most severe tests and have proved of highest value. The comparatively low power consumption of these efficient light-producers makes possible their use to outline landing fields for night-flying in a completely unmistakable manner, and even hundreds of feet of luminous neon tubing can be operated for this purpose, where needed.

Radon (radium emanation) belongs to the family of rare gases, being a homologue of xenon. Ramsay and Gray, with only a small fraction of a cubic millimeter of the gas at their disposal at any one time, found its atomic weight to be 223. According to the radium disintegration theory, the radium atom (at. wt. 226) loses an atom of helium (at. wt. 4) as an alpha particle, leaving behind an atom of radium emanation. Subtracting 4 from 226 we obtain 222, the atomic weight of radon, a number in close agreement with the number found by Ramsay and Gray. Radon can be condensed to a phosphorescent liquid which boils at -62° . The element was formerly termed *niton* (Lat. *nitens*, shining).

Radon has a molecular weight of about 222, and is therefore nearly eight times heavier than air. The gas is exceedingly rare.

All the inert gases give very characteristic spectra, are chemically inert, and show general resemblances and gradations in physical properties such as are seen in other families of elements.

EXERCISES

1. Show the relation of nitrogen to phosphorus. What other elements are related to these?

2. What important rôle does nitrogen play in nature and in industry?

3. Give the history and occurrence of nitrogen. How is pure nitrogen prepared for laboratory experiments? How is nitrogen prepared on an industrial scale?

4. Which weighs more, a liter of nitrogen prepared from a nitrogen compound, or a liter of "atmospheric nitrogen"? Explain. State the chemical properties of nitrogen, and illustrate so far as possible by means of equations. Mention three ways for the "fixation" of nitrogen.

5. How much nitrogen by weight and by volume, measured over water at 21°C . and 772 mm., could be prepared by heating 15 g. of ammonium dichromate?

6. Discuss the Cycle of Nitrogen in nature, pointing out the great importance of leguminous plants and of nitrogenous fertilizers. If you had a farm the soil of which was acidic and very deficient in plant food, state what practical steps you would take to restore its fertility. How would you test a soil for acidity?

7. Name the components which are present in the air in almost constant proportions. What other components are always present, but quite variable in amount? Name some accidental components of the atmosphere.

8. Explain how oxygen, nitrogen, and argon can be separated by chemical means.

9. How may carbon dioxide be removed from a specimen of air? Discuss the "balance" which is maintained between oxygen and carbon dioxide in the atmosphere.

10. How may water vapor be removed from air? Account for the formation of dew, fog, rain, etc. Why does one feel so uncomfortable on a hot, humid day? Explain the effect of ventilation or of a fan.

11. What part is played by microbes in the air? What is the difference between infectious organisms and saprophytic organisms?

12. Give proofs that the air is a mixture.

13. Give the names, symbols, and occurrence of the members of the helium family.

14. What facts led to the discovery of argon? What are the properties of the element?

15. By whom and when were helium, neon, krypton, and xenon discovered? How may these gases be prepared?

16. Arrange the elements of the helium family according to their atomic weights, and enumerate, in tabular form, a number of their properties.

17. Show that the lifting power of helium is about 92 per cent that of hydrogen, *i.e.*, for balloons inflated with these gases and allowed to rise in the air.

18. Outline the Hampson process for the production of liquid air. Should a perfect gas expanding into a vacuum fall in temperature? Explain. Why does a bicycle pump heat up when it is operated?

19. Compare and contrast the properties of the inert gases with those of the alkali metals (sodium and potassium) and with the halogens.

20. Would the assumed structure of the neon atom lead you to believe that it is a particularly stable system? Explain.

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CHAPTER XXI

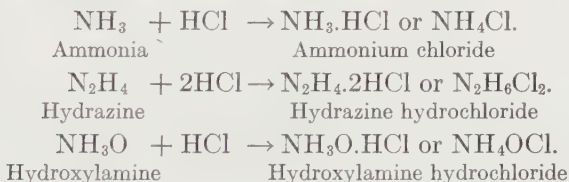
COMPOUNDS OF NITROGEN WITH HYDROGEN AND WITH THE HALOGENS

373. **Hydrides of Nitrogen.** — Nitrogen forms several hydrides, three of which are as follows:

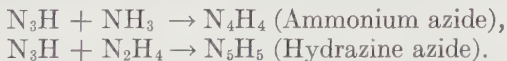
Ammonia,	NH_3
Hydrazine,	N_2H_4
Hydrazoic acid,	N_3H or HN_3 .

Hydroxylamine, NH_3O or NH_2OH , is an oxidized hydride.

Both ammonia and hydrazine are basic in character, dissolving in water to form alkaline solutions; they combine with acids to form salts. Hydroxylamine also forms salts with acids:



Hydrazoic acid, N_3H , has pronounced acid properties and therefore unites with bases, forming salts called *azides*:



These azides may be classed as hydrides of nitrogen.

Ammonia is by far the most important of these compounds.

AMMONIA, NH_3

374. **History.** — The early alchemists were acquainted with ammonium carbonate, which gives off ammonia when it dissociates. In early times sal-ammoniac (ammonium chloride) was produced by heating urine and common salt together; also from the soot

obtained by burning camel's dung. The compound was prepared subsequently by the destructive distillation of animal refuse, such as bones, hoofs, and horns, carbonate of ammonia being formed, which was converted into sal-ammoniac by the addition of hydrochloric acid. Owing to this mode of preparation, the old name for ammonia was "spirits of hartshorn." Priestley (1774) discovered gaseous ammonia, but previously it was known in the state of aqueous solution. Berthollet determined the composition of ammonia in 1785, and Faraday liquefied it in 1823.

375. Sources. — There are a number of sources of ammonia:

(1) *Atmospheric nitrogen.* In the nitrogen of the air we have an inexhaustible source of ammonia.

(2) *By the destructive distillation of soft coal.* Coal contains from 0.80 to 2.4 per cent of nitrogen, and when it is subjected to destructive distillation, "ammoniacal liquors" are obtained. This is a great industrial source of ammonia.

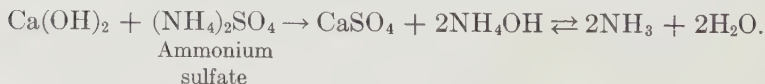
(3) *Ammonia is formed by the decay of nitrogenous organic matter.* A small amount of the gas finds its way into the air where it combines with nitric acid (produced by electrical discharge) to form ammonium nitrate, which is carried down by rain.

(4) *By the destructive distillation of nitrogenous animal matter: e.g., from horn, bones, etc.*

376. Preparation and Manufacture. —

(I) **Laboratory Method.** Ammonia is usually prepared in the laboratory by treating an ammonium salt with slaked lime (calcium hydroxide) or

other strong base. The salt and base interact by double decomposition to form another salt and ammonium hydroxide, and the latter dissociates into ammonia and water:



The gas can be expelled by heat and collected by the downward displacement of air (Fig. 126); it is dried by passing it through a tower containing quicklime. Large quantities of ammonia may be produced by this method, and stored in the form of liquid.

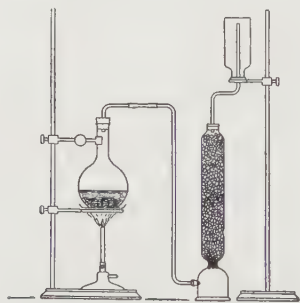
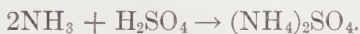


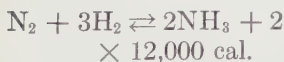
FIG. 126.

(II) **From Soft Coal.** The "ammoniacal liquor" is heated in a vessel with lime and the distillate collected in sulfuric acid:



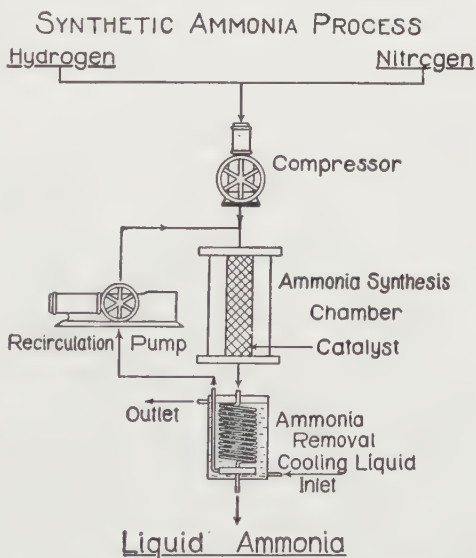
This salt may be obtained by evaporation of the solution until crystallization sets in. A ton of coal ordinarily yields about 20 pounds of ammonium sulfate. Ammonia is one of the valuable products obtained in the manufacture of coke by the by-product coke oven. In the year 1917, Germany produced about 300,000 tons of ammonium sulfate from her coke ovens. Ammonium sulfate is used chiefly as a fertilizer.

(III) **Synthetic Ammonia (The Haber Process).** Ammonia is manufactured (Fig. 127) by passing into a strong steel bomb a mixture of nitrogen and hydrogen, at a pressure between 150 to 200 atmospheres, over a suitable catalyst, such as some form of iron, or iron and molybdenum, at a temperature of about 500° . The reaction is reversible and exothermic:



It should be noted that four volumes of the interacting gases yield only two volumes of gaseous ammonia.

In accordance with van't Hoff's law (218), ammonia dissociates with increasing temperature; consequently the gases must not enter the catalyst chamber at too high a temperature (500 to 600°). The reaction products, with a working pressure in the neighborhood of 200 atmospheres, contain only a few per cent of ammonia (not above 14), depending on the various factors, so the unchanged



*Courtesy, Fixed Nitrogen Research Laboratory,
Washington, D. C.*

FIG. 127. Diagrammatic Representation of the Manufacture of Ammonia.

gases must be recovered. The ammonia is partially removed from the nitrogen and hydrogen by liquefaction or by absorption in water, the gases dried, passed over palladium asbestos to remove any traces of oxygen, and then returned to the catalyst furnace. The pressure is maintained by the admission of fresh gas. Osmium and uranium may also be used as catalysts, but these are too rare and expensive for technical use. The uranium catalyst is also readily "poisoned."

The Fixed Nitrogen Research Laboratory of Washington, D. C., has discovered a catalyst by means of which about 14 per cent of ammonia may be obtained. The catalyst is composed of iron and the oxides of potassium and aluminium in the form of potassium aluminate.

If a low temperature be employed, the formation of ammonia is too slow. On the other hand, if the temperature be too high, the yield of ammonia is reduced. Since the combined volumes of the nitrogen and hydrogen are double that of the ammonia (under the same conditions), the yield of ammonia is increased by the application of high pressures. (Explain as fully as you can.)

Several other processes are now undergoing technical development. The Claude process in France employs superpressures up to about 1,000 atmospheres. In Italy the Casale process is being operated, which, in essentials, is similar to the Haber process. In the United States a modified Haber process is being operated in the L'Azote plant at Belle, West Virginia. The process is carried out at 900 atmospheres with five catalyst units in series and with removal of liquid ammonia between each stage. The residual gas after the fifth unit is not further used.

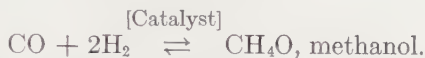
Nitrogen for the production of ammonia is obtained from liquid air, and the hydrogen from water gas ($\text{H}_2 + \text{CO} + \text{N}_2$), by electrolysis, or by the action of steam upon hot iron.

When water gas is employed, it is necessary to remove the carbon monoxide. The water gas used also contains nitrogen, as well as hydrogen and carbon monoxide. According to a recent development, the water gas is treated with steam in the presence of a catalyst, which transforms most of the carbon monoxide into carbon dioxide, hydrogen also being formed:



The gas now contains from 2 to 5 per cent of CO . The CO_2 is next scrubbed out, leaving a mixture of N_2 , H_2 , and the residual

CO. This mixture is passed over a suitable catalyst, which yields methanol (methyl alcohol, CH_4O or CH_3OH) a valuable product, which is condensed to a liquid:



Nitrogen and the remaining hydrogen are now passed into the steel bombs for conversion into ammonia. It is easy to see that this is an economical process. By far the greater part of hydrogen for synthetic ammonia is obtained from water gas. The preparation of ammonia by synthesis is one process for the fixation of nitrogen.

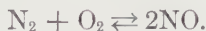
(IV) **The Cyanamide Process** (The Frank and Cario Process). This process depends upon the decomposition of calcium cyanamide, CaCN_2 (544), by the action of superheated steam:



The product is very pure, and a yield of 96 to 97 per cent is claimed.

The great cyanamide plant at Muscle Shoals has a rated annual capacity of 40,000 tons of fixed nitrogen. This is a second chemical process for the fixation of nitrogen.

We also have seen that nitrogen may be fixed by bacteria and by electrical discharge (arc process), in the latter case nitric oxide (NO) being formed:



377. The Fixation of Nitrogen. — It has been pointed out that nitrogen is closely related to fertilizers and therefore to agriculture. About half of the nitrogen for fertilizer mixtures is derived from inorganic sources, the chief of which are Chile saltpeter (NaNO_3) and the air.

Sir William Crookes, in his famous address delivered before the British Association, in 1898, had the prevision to state that there would be a shortage of nitrogenous fertilizer, so necessary for the growth of wheat, unless the chemist should devise ways and means of bringing about the chemical union of nitrogen with other substances.

As far back as 1892, Crookes performed, in the presence of the Royal Society, an experiment on the flame of burning nitrogen, which consisted in passing a powerful induction current between terminals, the nitrogen of the air burning to produce oxides which interacted with water to form nitric and nitrous acids. This soon

led to an important process for the production of nitric acid and nitrates.

As we have seen, there are several other methods for the fixation of nitrogen, the most important of which is the production of synthetic ammonia.

The fixation of nitrogen by chemical processes has increased enormously since 1913, the year before the beginning of the Great War, as shown by the table below.

WORLD'S FIXATION OF NITROGEN IN METRIC TONS

	1913	1917	1923
Direct synthetic.....	7,000	110,000	240,000
Cyanamide.....	34,000	230,000	140,000
Arc.....	14,000	35,000	36,000
Total.....	55,000	375,000	416,000

During the year 1924-25 the production of fixed nitrogen was over 500,000 metric tons (1 metric ton equals 1,000 kilograms, or 2,205 pounds), about 325,000 tons (65 per cent) being by the Haber process, 140,000 tons by the cyanamide process, and 36,000 tons by the arc process.

The tonnage of nitrogen compounds used as fertilizer for the years 1913 and 1927 is as follows:

1913	Tons N	1927	Tons N
Chilean nitrate.....	429,897	Synthetic ammonia...	700,000
By-product ammonia....	319,667	Cyanamide.....	200,000
Synthetic ammonia.....	90,491	Norwegian saltpeter..	30,000
	840,055		930,000

It should be added that in 1927 by-product sulfate of ammonia furnished 370,000 tons of nitrogen and Chilean nitrate 320,000 tons, making the total consumption 1,620,000 tons. The United States consumed about 300,000 tons. In 1927, the production of synthetic ammonia in America was 18,000 tons, but it is expected to exceed 80,000 tons in 1929 and in 1930, 140,000 tons.

By far the greatest part of atmospheric nitrogen is now fixed by the Haber process or its modification. In order for the other processes to compete with the Haber process, it is necessary to have cheap power.

In 1913, the year before the war, Germany imported over 600,000 tons of Chilean nitrates; but in 1925 only a little more than 24,000 tons were purchased, which means that Germany has developed an enormous air-nitrogen fixation industry. In 1924, the total exports of nitrates from Chile were over 2,300,000 tons; and in 1925 the United States imported 1,112,000 tons of nitrates, virtually all from Chile, and valued at over \$52,500,000.

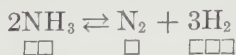
An immense quantity of ammonium sulfate, also extensively utilized as a fertilizer, is produced from the ammonia obtained as a by-product from coke- and gas-plants.

For several years our exports of ammonium sulfate have averaged over 125,000 tons annually, the value of which is much greater than that of our exported phosphate rock and superphosphates.

378. Physical Properties of Ammonia. — Ammonia is a colorless gas with a pungent odor and a caustic taste. The density of the gas (air = 1) is 0.5971. The C.T. is 132.9° and the C.P. 112.3 atmos. Ammonia forms a colorless liquid which boils at -33.2° and freezes at -77°, forming white crystals. The gas is extremely soluble in water. At S.T.P., one vol. of water absorbs about 1,300 vols. of NH_3 . This may be shown by filling a *heavy* round-bottomed flask nearly full of water to which a small quantity of red litmus solution has been added, and then connecting this flask with a similar flask filled with dry ammonia gas. By forcing a drop of water into the upper flask (see Fig. 108 for details), a fountain is produced. The solution turns from red to blue, for ammonium hydroxide is formed.

An aqueous solution of ammonia having a sp. gr. of 0.8844 contains 36 per cent of NH_3 . This solution is known as "concentrated ammonia." By boiling the solution the gas may be completely expelled. The dissolving of ammonia in water does not follow Henry's law (168), for some of the ammonia molecules unite with water molecules to form ammonium hydroxide (chemical change). The law does not hold for very soluble gases.

379. Chemical Properties. — Ammonia is not a very stable compound; it dissociates almost completely at 700°:



Ammonia also dissociates when electric sparks are passed through the gas. This may be readily accomplished by confining dry ammonia in the closed limb of a siphon eudiometer and then

passing a discharge of electricity through the gas (Fig. 128). At equilibrium, from 94 to 98 per cent dissociation occurs, the volume of gas being practically doubled. This experiment is important in determining the composition of ammonia.

Under ordinary conditions ammonia is said to be a non-combustible gas, but it may be burned in air by means of a special device. When a jet of the gas is allowed to flow into an atmosphere of oxygen, it may be ignited, burning with a yellowish flame:



Ammonia unites most readily with acids, forming **ammonium salts** (380):

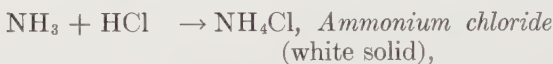


FIG. 128.

The formation of a cloud of ammonium chloride may be shown by sucking the two gases into a large glass globe.

Ammonia also unites with water to form *ammonium hydroxide*, a weak, unstable base:



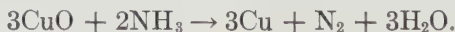
In an aqueous solution of ammonia, the ammonium hydroxide is in equilibrium not only with ammonia and water, but with the ions NH_4^+ and OH^- .

From concentrated solutions of ammonia it is possible to crystallize out two *hydrates*:

Ammonium hydroxide, $\text{NH}_3 \cdot \text{H}_2\text{O}$ or NH_4OH , m.p., -79° ; and Ammonium oxide, $2\text{NH}_3 \cdot \text{H}_2\text{O}$ or $(\text{NH}_4)_2\text{O}$, m.p., -79° .

Ammonia interacts with oxygen to form nitric oxide. This action occurs when a mixture of NH_3 and air is heated in the presence of platinum as a catalyst (see Nitric Acid).

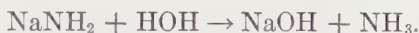
Ammonia, when heated, is a reducing agent, due to the hydrogen liberated. Thus, hot cupric oxide may be reduced in a tube by passing NH_3 over it:



When ammonia gas is passed over hot sodium or potassium, sodamide (NaNH_2) or potassamide (KNH_2) is formed:



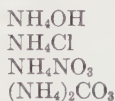
These *amides* are white crystalline compounds which are hydrolyzed by water:



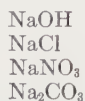
Ammonia gas is somewhat poisonous; air containing only a small fraction of one per cent may produce serious consequences when breathed.

380. Ammonium Compounds. — The *ammonium radical* (NH_4) is univalent, and it plays the rôle of a metal (see Alkali Metals). Thus, it may take the part of an atom of sodium in the formation of a base and salts, as the following formulae show:

Ammonium Compounds



Sodium Compounds



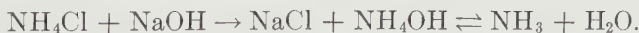
The corresponding compounds are similar in most respects, but ammonium salts are quite unstable when heated, decomposing to give a variety of products. Thus *ammonium chloride* gives HCl and NH_3 :



When NH_4Cl (sal-ammoniac) is used in soldering, the hot iron dissociates the salt, and the HCl removes the coat of oxide from the surface of the metal.

Ammonium carbonate, $(\text{NH}_4)_2\text{CO}_3$, also yields NH_3 when it dissociates; but when ammonium nitrite is heated nitrogen is formed, while ammonium nitrate yields nitrous oxide (N_2O).

When ammonium salts are warmed with an alkali, the odor of ammonia may be observed:



This is a good test for ammonium salts.

The *Nessler test* for ammonia is a very delicate one. Nessler's

reagent¹ contains potassium mercuric iodide, K_2HgI_4 , which interacts with ammonia to form the highly colored compound, Hg_2NI :



381. Uses of Ammonia. — Ammonia in the liquid state is employed very extensively as a refrigerant. When 1 g. of the liquid evaporates, 258 calories are used up (heat of vaporization of ammonia). In the manufacture of ice, liquid ammonia is allowed to

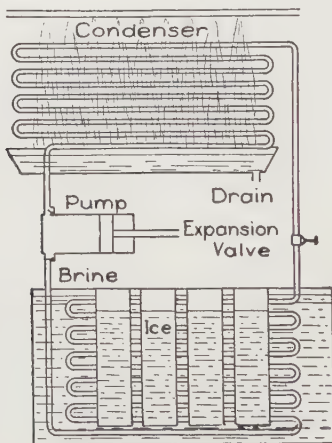


FIG. 129.

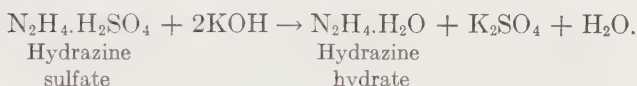
evaporate in metal pipes surrounded by brine made by dissolving calcium chloride in water. Cans containing water are immersed in the brine until ice is formed (Fig. 129). The gaseous ammonia is compressed and cooled, and used again to produce ice. Ammonia is also used for the manufacture of explosives, soda, fertilizers, ammonium salts, nitric acid (387), ammonium hydroxide ("ammonia water"), etc. "Household ammonia" is made by dissolving NH_3 in water; it is used extensively as a cleansing agent.

¹ Nessler's reagent can be prepared as follows: Dissolve 35 g. of KI in about 200 cc. of pure water, and then add a strong solution of $HgCl_2$ until a faint show of excess is indicated. 160 g. of solid KOH are now added, and the solution diluted to 1,000 cc. A strong solution of $HgCl_2$ is added, little by little, until the red HgI_2 just begins to be permanent. Finally, allow the precipitate to settle, but do not filter. The reagent should have a pale straw color, and it is improved by age.

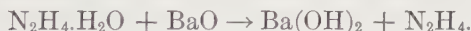
Ammonium salts are used in soldering, in dry batteries, as fertilizers, etc.

382. Other Hydrides of Nitrogen. — **Hydrazine**, N_2H_4 , is a diacid base containing two univalent amine radicals (NH_2), and is sometimes called diamine, $\text{H}_2\text{N} - \text{NH}_2$. It may be derived from ammonia by removal of hydrogen. This may be accomplished by adding sodium hypochlorite (NaClO) to strong ammonia containing glue; the solution is then concentrated and sulfuric acid added, whereupon hydrazine sulfate, $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$, is obtained in the form of white crystals.

By treating hydrazine sulfate with caustic potash, hydrazine hydrate is obtained:

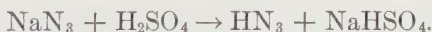


Hydrazine hydrate is a powerfully corrosive, colorless, fuming liquid, with an odor similar to that of ammonia. By heating hydrazine hydrate with barium oxide, hydrazine is obtained:

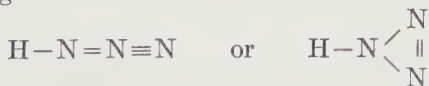


Hydrazine boils at 113.5° . It forms a hydrate with water, salts with acids, is an active reducing agent, and very poisonous.

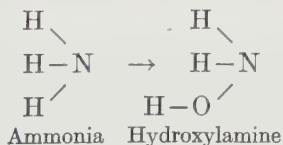
Hydrazoic Acid, HN_3 , can be prepared by distilling a salt of the acid, such as sodium azide (NaN_3), with dilute sulfuric acid:



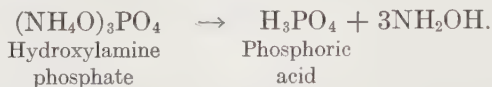
It is a colorless liquid, boiling at 37° . Its salts are termed **azides**, and many of them are explosive, as is the warm acid. The exact structure of the acid is unknown, but there are two possible ways of representing it:



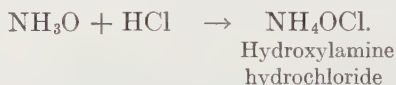
Hydroxylamine, NH_3O or NH_2OH , may be regarded as a molecule of ammonia in which one hydroxyl radical has taken the place of an atom of hydrogen:



It can be prepared by heating the phosphate, $(\text{NH}_4\text{O})_3\text{PO}_4$, under reduced pressure:



Hydroxylamine is a white solid which melts at 33° and boils at 58° , the pressure being 22 mm. It combines with acids to form salts (see ammonium chloride, NH_4Cl , etc.):



383. Halogen Compounds of Nitrogen. — It is of interest to know that when a solution of NH_4Cl is treated with an excess of chlorine, drops of an oily liquid, *nitrogen trichloride* (NCl_3), may be obtained:



This compound was first prepared by Dulong (1811). It is an oily liquid of pale-yellow color, and extremely explosive. Dulong lost an eye and three fingers in preparing it, and Faraday and Davy were also injured in conducting experiments with the substance.

Nitrogen iodide, $\text{NI}_3 \cdot \text{NH}_3$, may be prepared by treating iodine dissolved in KI solution with concentrated ammonia. The compound is obtained in the form of a brown precipitate. It may be handled while wet; but when dry it explodes with great violence, liberating iodine, as well as nitrogen. The gentle touch of a feather, or possibly the tread of a fly, is sufficient to explode it.

EXERCISES

1. Name two hydrides of nitrogen and show their relationship, stating whether they are basic or acidic.
2. Outline the history and sources of ammonia. What are the great commercial sources of the compound?
3. Outline (including chemical equations) the following methods for preparing ammonia: (1) laboratory method; (2) from coal; (3) the Haber process; (4) the cyanamide process.
4. In the manufacture of ammonia by the Haber process, show how the equilibrium may be displaced backward and forward. Show that we have here an illustration of van't Hoff's law. Explain the effect of pressure in the synthesis of ammonia.

5. Starting with water gas containing nitrogen, show how the CO may be removed and ammonia produced from the residual gases.
6. Show the great economic importance of the fixation of nitrogen.
7. State the physical properties of gaseous and of liquid ammonia. Consult a reference book and point out as many analogies as you can between water and liquid ammonia.
8. State Henry's law. Why does not the dissolving of ammonia in water follow, as a rule, this law?
9. How did Faraday liquefy ammonia and other gases?
10. Starting with 1 kilogram of calcium cyanamide, what weight of ammonia could be produced from it? State all the necessary steps and write the equation.
11. How many different kinds of molecules and ions are there in a vessel containing "household ammonia"?
12. State five chemical properties of ammonia, and illustrate each by writing molecular equations.
13. Consult a work of reference and find out how ammonium amalgam is prepared. State its properties and uses.
14. How would you recognize an ammonium compound? Show by equations the products obtained when several different ammonium salts are heated.
15. State the principle involved when ammonia is employed as a refrigerant.
16. If 1 g. of water at 20° absorbs 0.526 g. of NH_3 , how much ammonium sulfate would be required to prepare enough of the gas to saturate 1 kilogram of water at 20°? What volume would the gas occupy at 25° and 745 mm.?
17. How can it be shown (1) that ammonia is extremely soluble in water; (2) that the solution contains ammonium hydroxide; (3) that ammonium chloride, when heated, yields HCl and NH_3 ; (4) why the formula of ammonia gas is given as NH_3 ; (5) that two volumes of ammonia form four volumes of gases on dissociating?
18. Discuss from the standpoint of chemical equilibrium and the ionic theory (1) the formation of ammonia when a solution of NH_4Cl is treated with one of NaOH ; (2) the interaction of a solution of ammonium hydroxide and sulfuric acid.
19. Give the names of the compounds having the following formulae: N_2H_4 , HN_3 , KN_3 , PbN_6 , $\text{N}_2\text{H}_4 \cdot \text{HNO}_3$, $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$, NH_2OH , NH_4K , $(\text{NH}_4\text{O})_3\text{PO}_4$, and $(\text{NH}_4)_3\text{PO}_4$.
20. How may hydrazine be prepared? What are its chief properties? How is it related to ammonia?
21. From the nature of hydrazoic acid and of azides in general, can you suggest a use for lead azide?

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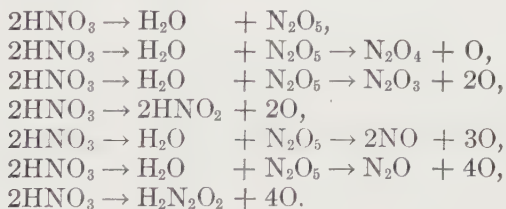
CHAPTER XXII

THE OXIDES AND OXYGEN ACIDS OF NITROGEN

384. **Oxides and Oxyacids of Nitrogen.** — The following oxides and oxyacids of nitrogen are known:

Nitrous oxide,	$\text{N}_2\text{O} \leftarrow \text{H}_2\text{N}_2\text{O}_2$,	Hyponitrous acid
Nitric oxide,	NO	
Nitrogen trioxide,	$\text{N}_2\text{O}_3 \leftrightarrow \text{HNO}_2$,	Nitrous acid
Nitrogen tetroxide,	$\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$	(Polymers)
Nitrogen pentoxide,	$\text{N}_2\text{O}_5 \leftrightarrow \text{HNO}_3$,	Nitric acid

N_2O_3 and N_2O_5 interact with water to form acids, and when these acids are dehydrated they form the anhydrides. When hyponitrous acid loses the elements of water, N_2O is formed, but N_2O does not interact with water to form an acid. These substances may be derived from HNO_3 :



Nitrogen pentoxide is obtained by dehydrating nitric acid, and the other compounds are reduction products of the acid. Nitric acid is an active oxidizing agent.

NITRIC ACID. HNO_3 , OR $\text{HO}\cdot\text{NO}_2$

385. **History.** — Nitric acid (*aqua fortis*) was prepared by the alchemists, who used it as a reagent for separating silver from gold. Glauber was probably the first to prepare the acid from niter and sulfuric acid — a method of preparation still in use. Cavendish (1785) established the composition of nitric acid synthetically. He passed a discharge of electricity through oxygen

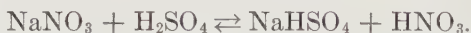
and nitrogen in the presence of water or alkaline solutions, which absorbed the oxides of nitrogen.

386. **Sources.** — The chief source of nitric acid is *sodium nitrate*, NaNO_3 , commonly called Chile saltpeter. This salt, mixed with other salts, occurs in large deposits in a rainless district in Chile and Peru. The deposit is 220 miles long, 2 miles wide, and about 5 feet thick; it contains from 20–75 per cent of NaNO_3 . The fact that the sodium nitrate is mixed with sodium chloride and other salts, probably indicates that the region was at one time covered by the sea.

Another source of nitric acid is *potassium nitrate*, KNO_3 , commonly known as saltpeter or niter. This compound is found especially in the neighborhood of oriental cities. We have seen (375) that when nitrogenous organic matter decays in the air ammonia is formed, the change being due to the action of bacteria. By the action of other bacteria and the oxygen of the air, ammonia is converted into nitric acid, which interacts with alkalis, such as potash or soda, to form nitrates. In the neighborhood of Oriental cities, KNO_3 has been formed from the decomposition of urea from urine in contact with the potash contained in the soil. Chile saltpeter may have been formed by the decomposition of sea plants and animals (245).

Another source of nitric acid is *atmospheric nitrogen*, which is inexhaustible. This will be discussed later. Nitric acid also may be obtained by the oxidation of ammonia.

387. **Preparation.** — (I) Nitric acid can be prepared by heating a nitrate with concentrated sulfuric acid. In the laboratory, as well as in the manufacture of the acid, sodium nitrate is commonly employed:



When the mixture of salt and acid is heated in a retort, the more volatile acid (B.P. 86°) is expelled, being collected in a cooled receiver. The laboratory method of preparation may be conducted as shown in Fig. 130.

The commercial preparation is carried out by heating the nitrate and sulfuric acid in an iron retort, and the vapor of nitric acid is condensed in receivers cooled by running water (Fig. 131). By using double the weight of sodium nitrate given in the equation above and heating the mixture to a higher temperature, the sodium bisulfate is converted into sodium sulfate:



Owing to the fact that the higher temperature partly decomposes the nitric acid, the process is not an economical one. The distillate obtained, even at the lower temperature, has a yellowish color, caused by the presence of NO_2 ; for when HNO_3 is heated, it is partially decomposed into water, oxygen, and nitrogen peroxide. Pure hydrogen nitrate may be obtained by heating NaNO_3 and H_2SO_4 in a retort under diminished pressure and cooling the vapor.

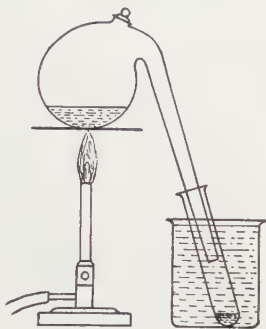


FIG. 130.

Sodium bisulfate, or "niter cake," which is a by-product of the manufacture of nitric acid, is used extensively in the bleaching, dyeing, and textile industries; in pickling and cleaning metals; and in the manufacture of hydrochloric acid (271).

(II) **Preparation from Air** (The Arc Process). — When electric sparks are passed through air or when air is passed through an electric arc, nitric oxide is formed. The reaction is both reversible and endothermic:

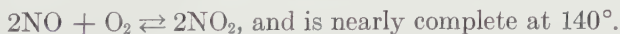


In accordance with the law of van't Hoff (218), high temperature should favor the production of NO (why?). This is found to be the case, as the following data show:

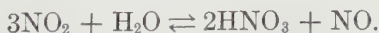
<i>Temperature C.</i>	<i>Per Cent of NO observed</i>
1265°	0.37
1487°	0.64
2034°	2.05

Even at 3,000° C. only about 5 per cent of nitric oxide is formed.

When the nitric oxide is cooled, it commences at 620° to unite with oxygen to form NO_2 :



The NO_2 now passes to the absorption towers where it interacts with hot water to form nitric acid:



The NO which is liberated interacts with oxygen of the air to form NO_2 , and the absorption cycle is continued.

The arc process has been developed on a large scale in Norway where abundant water power means cheap electricity. In the **Birkeland-Eyde process**, which is the most important of the arc processes, the electric arc is spread between the poles of an electro-

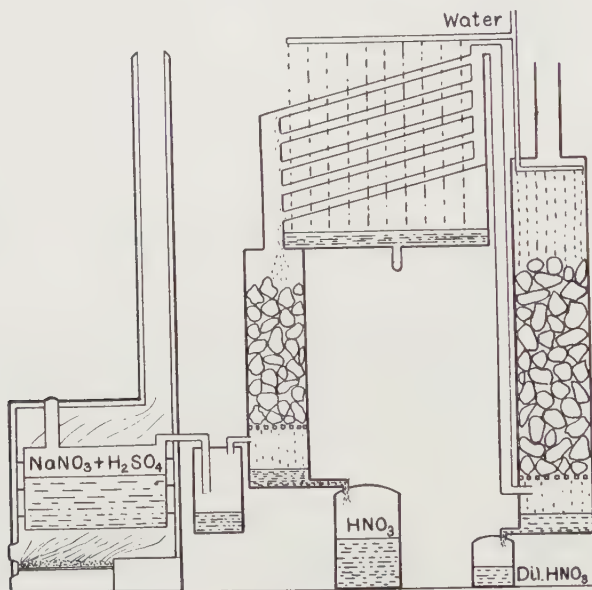


FIG. 131.

magnet. This process is quite efficient, for the arc is spread out into disks, so that large quantities of air come under its influence.

Figure 132 shows the manufacture of nitric acid from the atmosphere. Air is delivered to the electric furnace, *F*, by means of the pump, *P*. The mixture of nitric oxide and air now passes to the cooler, *C*, where the temperature is materially lowered. From the cooling chamber the gases are passed under the boilers, *B*, to generate steam and further to cool the gases. They are now passed into the oxidation chamber, *D*, where NO_2 is formed. Next, the gases are passed through the absorption tower, *T*, where NO_2 and water interact to produce HNO_3 and NO . Nitric acid is drawn off at the bottom of the tower; and by allowing it to flow on a bed of limestone, calcium nitrate is formed. NO and the excess of air escape at the top of the tower, the NO combining of course with O_2 to form more NO_2 . This residual NO_2 may be absorbed in weak alkali solution.

The dilute solution of nitric acid obtained by this process is used to some extent in preparing nitrates. Thus, Norway as far back as 1909 produced 9,422 tons of calcium nitrate.

According to the **Schönheer process**, which is also employed in Norway, air is sent through a tube 22 feet long, and as it

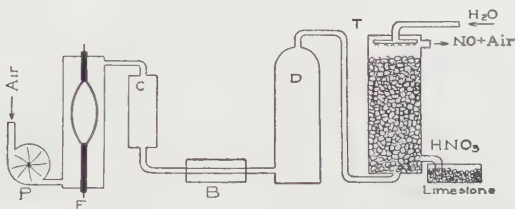
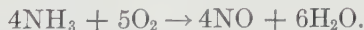


FIG. 132.

traverses the tube the column of air rotates, thus exposing every part to the electric discharge.

In Italy and Austria the Pauling process is employed. Pre-heated air is used, and while the discharge is different, the principles upon which the process is based are the same as those employed in the other processes.

(III) **Preparation from Ammonia** (Ostwald Process). A mixture of 10 vols. of air to 1 vol. of ammonia is passed through a nickel tube containing a roll of corrugated platinum foil which acts as a catalyst. Modern technical units now employ several layers of incandescent platinum gauze through which the ammonia-air mixture is forced at high velocity (Fig. 133). The reaction is exothermic and the temperature of the platinum gauze is maintained at 800° – $1,000^{\circ}$. The gaseous products consist of nitric oxide, nitrogen, and the residual oxygen from the air. The reaction which occurs is represented by the following equation:



The gases are cooled down and NO is oxidized to NO_2 , after which they are passed into the nitric acid absorption towers (see the Arc Process). The catalyst is poisoned by dust, etc., being rendered ineffective. To guard against this, the gases are carefully purified. A conversion efficiency as high as 95 per cent has been obtained.

This process was largely developed in Germany before and during the Great War, which enabled that country to produce



FIG. 133. Interior of Catalyzer Building, United States Nitrate Plant No. 2, Muscle Shoals, Ala.
In each of the vertical tanks a mixture of ammonia and air is passed through layers of platinum gauze, nitric oxide (NO) being produced.

Courtesy of War Department.

great quantities of nitric acid after the supply of Chile saltpeter was exhausted. At the present time, nitrous fumes required for the manufacture of sulfuric acid are produced by the oxidation of ammonia.

388. **Properties.** — Hydrogen nitrate is a colorless liquid which boils at 86° and has a sp. gr. of 1.52. The liquid may be frozen to a snow-like solid, which melts at -47° . When hydrogen nitrate is distilled, a portion of the compound decomposes and the acid becomes constantly weaker until it contains 68 per cent of NHO_3 , when the liquid boils unaltered at 120.5° , yielding an acid having a sp. gr. of 1.414 at 15.5° . In case an acid more dilute than this is distilled, its concentration rises until it contains 68 per cent of HNO_3 and boils at constant temperature (see Hydrochloric acid, 293). The concentrated nitric acid of commerce contains about 68 per cent of HNO_3 . "Fuming" nitric acid is the concentrated acid containing nitrogen tetroxide in solution.

389. **Chemical Properties.** — (1) *Nitric acid is not very stable in sunlight and when heated:*

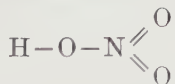


(2) *Hydrogen nitrate is an extremely corrosive liquid;* it attacks the skin, producing painful wounds, and is employed in surgery as a cauter. The diluted acid colors the skin, nails, wool, silk, etc., yellow.

(3) *Nitric acid is a strong monobasic acid,* being one of the most highly ionized:



The graphic formula of the acid may be written thus:



(4) *It is a powerful oxidizing agent* and very commonly decomposes, in the presence of an oxidizable material, virtually as follows:



Two molecules of the compound contain, therefore, three atoms of oxygen available for oxidation. By its action, carbon may be oxidized to carbon dioxide, sulfur to sulfuric acid, phosphorus to

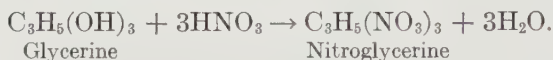
phosphoric acid, etc. Fuming nitric acid is a more powerful oxidizing agent than is concentrated nitric acid. The great activity of this reagent may be shown by pouring a little concentrated sulfuric acid into fuming nitric acid and then carefully pouring in 1–2 cc. of turpentine, which ignites.

(5) *Aqua Regia*. This reagent is prepared by mixing 1 vol. of concentrated nitric acid and 3 vols. of hydrochloric. The acids interact to form chlorine and nitrosyl chloride (NOCl):



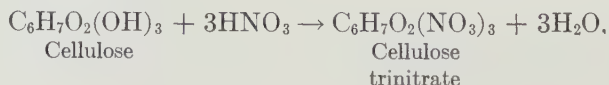
It is a powerful oxidizing agent and solvent. Thus, it readily dissolves gold and platinum. This reagent was well known to the alchemists, who called it *aqua regia* on account of its great solvent action.

(6) *Nitric acid interacts with glycerine to form nitroglycerine*. Since water is formed in this reaction, concentrated sulfuric acid is mixed with 98 per cent nitric acid. The chemical change is as follows:



The name nitroglycerine is a misnomer, for the compound does not contain the nitro group (NO_2). Its correct name is *glyceryl trinitrate*. **Nitroglycerine** is an explosive liquid, which is used in the manufacture of dynamite. The compound was discovered by the Italian chemist, Sobrero, in 1846, and in 1864 Nobel began its manufacture on a large scale. Nobel invented **dynamite**, in 1866, by absorbing nitroglycerine in diatomaceous earth (German, *Kieselguhr*). Nitroglycerine is exploded by shock, producing enormous volumes of gases. It is used in the liquid state for "torpedoing" oil and gas wells. It is now common to prepare dynamite by absorbing nitroglycerine in ammonium nitrate instead of kieselguhr.

(7) *Nitric acid interacts with cellulose (cotton)*. **Nitrocellulose** or **guncotton** is manufactured by treating cellulose fiber (cotton) with a mixture of concentrated nitric and sulfuric acids (Fig. 134). The compound formed is now regarded as a nitrate of cellulose. When the nitration is thoroughly carried out, cellulose trinitrate (guncotton) is formed:



Guncotton looks very much like cotton. It is exploded by a detonating cap, and when unconfined it burns rapidly, producing a large flame. Guncotton is used in torpedoes and mines and as the basis of certain smokeless powders. It was discovered by Schönbein in 1845. In 1865 Abel improved the process of manufacture, and at the present time it is considered one of the safest of explosives, provided that it is properly manufactured.



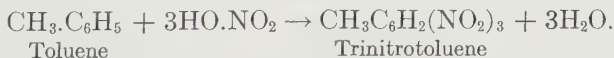
Courtesy, Eastman Kodak Co.

FIG. 134.

Battery of Machines for Nitrating Cotton.

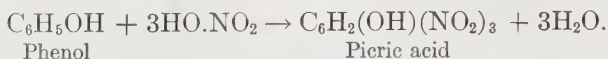
When cellulose is less thoroughly nitrated, **pyroxylin**, or "collodion-cotton," is obtained. It dissolves (colloidal solution) in a mixture of alcohol and ether, forming **collodion**. When collodion is heated with mildly alkaline agents, the viscosity of the liquid is lessened, so that a solution of it can be sprayed on a surface such as that of an automobile, giving an excellent coating of nitrocellulose lacquer. One such lacquer is known as "Duco." Pyroxylin is used very extensively in the manufacture of collodion, artificial leather and silk, celluloid, smokeless powder, blasting gelatine, etc. **Celluloid** is produced on a large scale by mixing pyroxylin with camphor and a little alcohol and passing the material between rollers.

(8) *Nitric acid acts on toluene to form trinitrotoluene (TNT)*, one of the most important of explosives:



Trinitrotoluene is a solid, which melts at 81.5°. It is used for filling "high explosive" shells. The compound is not easily exploded by shock during transportation, but can be exploded readily by a detonator. Before the close of the Great War, large quantities of ammonium nitrate were being mixed with the more expensive TNT. The mixture is an excellent explosive.

(9) *Nitric acid and phenol ("carbolic acid") interact to form picric acid, or trinitrophenol:*



Picric acid is a yellow, crystalline compound, which is used as an explosive. It, like TNT, can be melted safely and poured into shells. The alkaline salts of this acid are powerful explosives, but are too dangerous to be employed as such. Picric acid was discovered by J. A. Glauber, in the seventeenth century. He obtained it by treating wood with concentrated nitric acid. It was perhaps the first chemical body known to be explosive, and long ago was employed as a yellow dye. In 1871, Sprengel discovered that picric acid may be detonated by fulminate of mercury. The British call it *lyddite*, while the French call it *melinite*. The latter used great quantities of it during the recent war.

Guncotton and nitroglycerine are the two basic substances employed in modern smokeless powder and in dynamite. Trinitrotoluene (TNT), picric acid, and ammonium nitrate are also utilized as explosives. It is interesting to know that all these compounds contain either the nitrate ($-\text{NO}_3$) or the nitro ($-\text{NO}_2$) group, and are therefore either nitrate or nitro bodies. They may be represented by the general formulae $\text{R}\cdot\text{O}\cdot\text{NO}_2$ and $\text{R}\cdot\text{NO}_2$, in which R stands for a carbon complex. None of them can be produced without nitric acid. Under ordinary conditions they are relatively stable bodies, but are capable of breaking down or exploding when subjected to slightly changed conditions, such as mechanical shock. When a high explosive, such as guncotton or nitroglycerine, breaks down, the explosion or detonation is primarily the result of *internal combustion*. Thus, the nitroglycerine molecule, $\text{C}_3\text{H}_5(\text{NO}_3)_3$, contains nine atoms of oxygen, which are sufficient to change all the carbon to oxides and the hydrogen to water. It also is of interest to know that these *explosives are endothermic compounds*; indeed, most carbon and nitrogen compounds are endothermic. Carbon dioxide is, however, exothermic and, like water and lime, is very different from explosives.

Dynamite is too sensitive and violent for use in guns and shells. It is employed on a large scale for blasting and wrecking purposes.

Blasting gelatin is prepared by dissolving one part of pyroxylin in nine parts of nitroglycerine. It is used for blasting and for the manufacture of smokeless powders.

Cordite is a smokeless powder produced by incorporating gun-cotton with nitroglycerine, and dissolving in acetone. A little vaseline is added to prevent corrosion of the guns. When the acetone is evaporated, solid cordite is left.

According to C. L. Reese, smokeless powders for rifled arms may be divided into two classes — *nitroglycerine powders*, consisting of nitroglycerine and nitrocellulose, and *nitrocellulose powders*, consisting of nitrocellulose only. Virtually all smokeless powders when burned are transformed into gases, principally carbon monoxide, carbon dioxide, nitrogen, and water vapor, all of which are colorless and hence invisible.

High explosives did not come into general use until after the close of the Civil War. According to Reese, if the Great War had continued, the United States could have manufactured 1,000,000,000 pounds of smokeless powder during the year 1919. While war calls for a greatly increased supply of explosives, these are used in tremendous quantities in times of peace, the normal domestic consumption amounting to more than 500,000,000 pounds per annum, while during the late war our annual production of all military explosives was perhaps from 2,000,000,000 to 3,000,000,000 pounds.

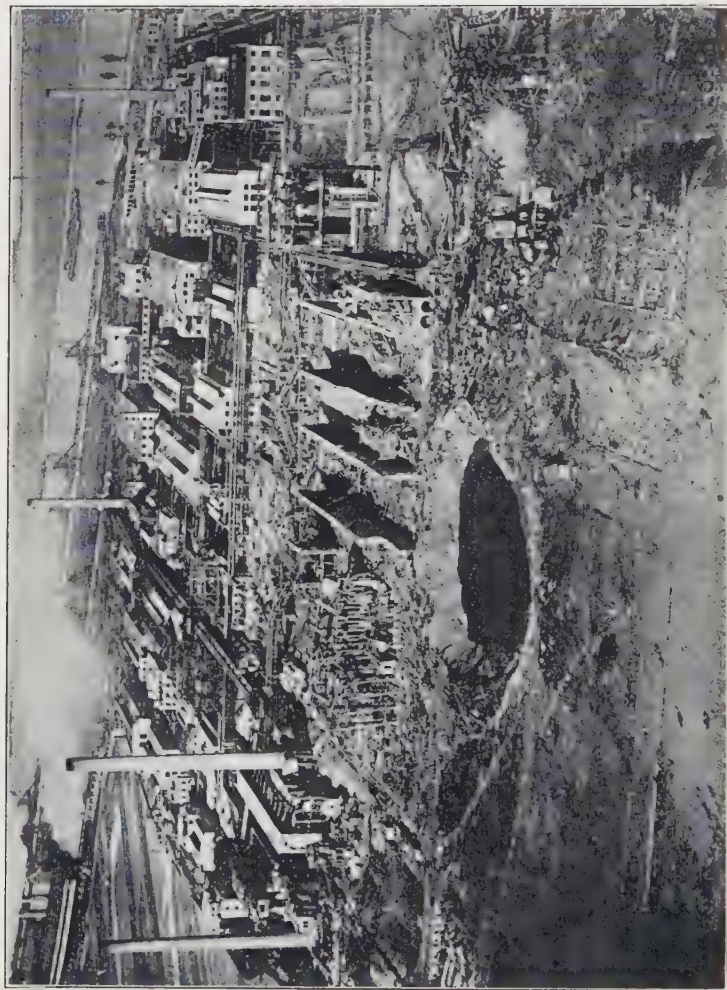
Figure 135 illustrates the terrific explosion at Oppau, Germany.

390. Nitric Acid a Powerful Solvent and Oxidizing Agent. — In order to understand the chemical conduct of nitric acid, it is important to know that the valence of nitrogen varies from +5 to -3:



When metals and non-metals are treated with nitric acid, it is possible to obtain many different products, which depend upon the nature of the element, the concentration and temperature of the acid, etc. *In general, when nitric acid is employed as an oxidizing agent, the more active the reducing agent the greater will be the change in the valence of nitrogen; also, the more dilute the nitric acid, the greater is the change in valence of nitrogen.* Nitric acid interacts with most of the metals. Gold and platinum and a few of the rare metals are exceptions.

When the metals in the electromotive series preceding hydrogen are treated with dilute nitric acid, hydrogen is displaced as it is from other acids. If the metal is more active than zinc (*e.g.*, Mg) a considerable part of the hydrogen escapes oxidation. In the case of zinc and less active metals, most or all of the hydrogen is oxidized to water.

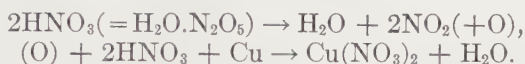


Courtesy of Underwood and Underwood.

Fig. 135. Explosion at Oppau.

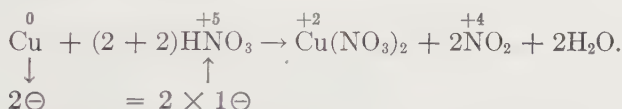
The photograph for this illustration was taken from an airplane the second day after the explosion which wrecked the Badische Aniline Works at Oppau, Germany, in 1921. A hole 250 feet in diameter and over 50 feet deep was formed in the earth.

When copper is dissolved in nitric acid of sp. gr. 1.4, nitrogen peroxide (NO_2) is formed:

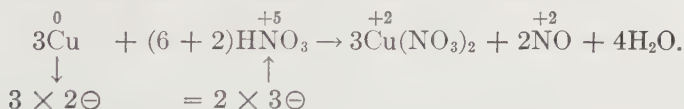


When copper is dissolved in nitric acid of sp. gr. 1.2, nitric oxide (NO) is formed.

The equations showing the action of nitric acid upon copper may be balanced by the electron method (263). For the concentrated acid we have:

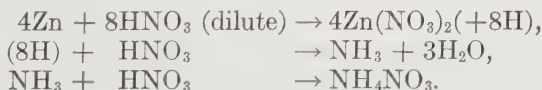


For the diluted acid the equation may be written thus:

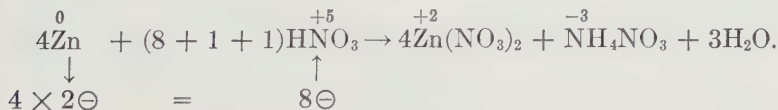


In the latter reaction the valence change in nitrogen was greater than in the former, which is an illustration of the principle stated above.

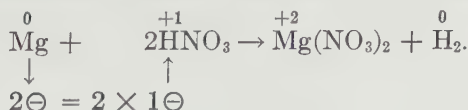
When zinc is dissolved in dilute nitric acid, some of the acid may be reduced to ammonia, which then interacts with excess acid to form ammonium nitrate:



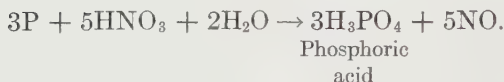
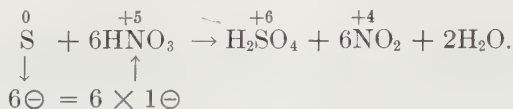
The equation may be balanced according to the electron method as follows:



Very active metals, *e.g.*, magnesium, not only may reduce the nitric acid to ammonia, but also the hydrogen-ion to free hydrogen:



Many non-metals, such as sulfur and phosphorus, are oxidized by nitric acid, acids being produced:



(Balance the last equation by the electron method.)

391. Uses of Nitric Acid. — About 75 per cent of the output of nitric acid is used in the manufacture of explosives; it also is used in the production of pyroxylin plastics, dyes and chemicals, lacquers, and as a solvent and oxidizing agent.

392. Nitrates. — The salts of nitric acid, or nitrates, are among the most important compounds known. Thus, *sodium nitrate* and *potassium nitrate* are valuable fertilizers and the chief source of nitric acid. *Ammonium nitrate*, NH_4NO_3 , is an important explosive. *Barium nitrate*, $\text{Ba}(\text{NO}_3)_2$, and *strontium nitrate*, $\text{Sr}(\text{NO}_3)_2$, are used in pyrotechny; and *silver nitrate*, AgNO_3 , is used in photography, the manufacture of indelible ink, as a cauter in medicine, etc.

In general, the normal nitrates are soluble in water and are decomposed by heat.

A nitrate (or nitric acid) may be recognized by the following test:

Dissolve a small quantity of nitrate in water, add an equal volume of concentrated sulfuric acid, and then cool the mixture to room temperature. Incline the test-tube containing the liquid, and carefully pour down its side a concentrated solution of freshly prepared ferrous sulfate, FeSO_4 , so that the liquids mix only at the surface of contact. A dark-brown ring appearing at the junction of the liquids indicates the presence of a nitrate. The sulfuric acid interacts with NaNO_3 to liberate HNO_3 which is reduced by FeSO_4 to nitric oxide (NO). The excess of FeSO_4 will then absorb NO to give a brown color — a delicate test for nitric acid or a nitrate.

393. Nitrous Acid and Nitrites. — Nitrous acid, HNO_2 , is not known in the free state, for the compound is very unstable. An aqueous solution containing the substance can be prepared by dissolving nitrogen trioxide (nitrous anhydride) in ice-cold water:



The solution has a beautiful blue color, and when it is warmed, HNO_2 rapidly decomposes.

The salts of nitrous acid are called **nitrites**, and they are, as a rule, very stable compounds. Nitrites may be formed by the reduction of nitrates. Thus, sodium nitrite may be prepared by fusing sodium nitrate, or by heating the compound with lead:



Potassium nitrate thus treated yields potassium nitrite.

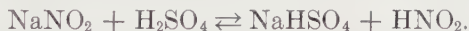
Nitrites can also be prepared by treating an alkali with nitrous fumes:



A mixture of NO_2 and NO may be regarded as being equivalent to *nitrous anhydride*:



When a dilute aqueous solution of a nitrite is acidulated, a pale-blue solution containing HNO_2 is obtained:



When the solution is warmed, the following change occurs:



When a concentrated solution of a nitrite is acidified, a brown gas is evolved at once. This reaction differentiates nitrites from nitrates.

NITROUS OXIDE, N_2O

394. Preparation. — *Nitrous oxide*, or *laughing gas*, was first prepared by Priestley in 1772, who obtained it by reducing nitric oxide (NO). The gas is prepared very readily by gently heating dry ammonium nitrate:



Owing to the fact that this reaction is exothermic, care must be exercised not to heat ammonium nitrate too rapidly nor too hot. The gas may be collected over warm water or mercury.

395. Physical Properties. — Nitrous oxide is a colorless gas having a faint, pleasant smell and sweet taste. Its sp. gr. is

1.53, its C.T. 36.5° , and its C.P. 71.65 atmos. At 0° , the gas liquefies under a pressure of 30 atmos. Liquid nitrous oxide is an article of commerce, being contained in strong cylinders. The liquid boils at -89.8° . Nitrous oxide is quite appreciably soluble in water. At 0° , 1 vol. of water dissolves 1.3 vols. of the gas, while at 25° only 0.596 vol. dissolves. The gas is more soluble in alcohol.

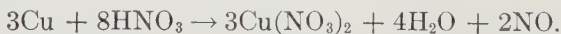
When nitrous oxide is inhaled by man and animals, it produces a remarkable effect. This physiological effect was first observed by Humphry Davy, who breathed 16 quarts of the gas, and afterwards wrote: "This gas raised my pulse upward of 20 strokes, made me dance about the laboratory as a madman, and has kept my spirits in a glow ever since."

Nitrous oxide is used as an anesthetic in cases of minor surgical operations, especially in dentistry. For use as such, it must contain neither nitric oxide nor chlorine; and, to prevent suffocation, it must be mixed with oxygen.

396. Chemical Properties. — Nitrous oxide is a supporter of combustion, but not as active as free oxygen. Thus, a glowing splinter and phosphorus will burn brilliantly in an atmosphere of the gas, forming oxides and free nitrogen. *Nitrous oxide, unlike oxygen, does not combine with nitric oxide (NO) to form red-brown fumes (100).* This test serves to distinguish the two gases.

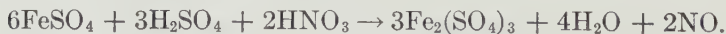
NITRIC OXIDE, NO

397. Preparation. — (1) Nitric oxide is usually prepared for laboratory use by dissolving copper turnings or copper foil in nitric acid having the sp. gr. of 1.2:



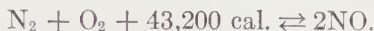
The gas is purified to a certain extent by passing it through water and caustic soda. It is collected over water. Nitric acid also interacts with zinc, mercury, silver, etc., to form nitric oxide.

The pure gas may be prepared by treating a solution of ferrous sulfate with sulfuric and nitric acids:



(2) We have seen that nitric oxide can be produced by subjecting a mixture of nitrogen and oxygen (air) to an electric

discharge (387):



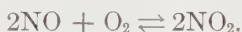
This is a very valuable method for the fixation of nitrogen.

398. **Properties.** — Nitric oxide is a colorless gas having a sp. gr. of 1.039 (air = 1). Its C.T. is -93.5° and its C.P. 71° atmos. It forms a colorless liquid, which boils at -150° . The gas is only slightly soluble in water.

Nitric oxide is the most stable of the oxides of nitrogen. When heated, decomposition begins at a faint red heat, but is only slight at 900° (387).

Nitric oxide will support the combustion of burning phosphorus, but burning splinters and sulfur are extinguished when introduced into the gas.

Nitric oxide combines most readily with free oxygen to form ruddy fumes of nitrogen peroxide:



A mixture of nitric oxide and the vapor of carbon disulfide burns with a beautiful blue flame which is rich in actinic rays.

NITROGEN TETROXIDE

399. **Preparation.** — *Nitrogen tetroxide* (sometimes called “nitrogen peroxide” or “nitrogen dioxide”) is prepared by heating the nitrate of a heavy metal (usually lead nitrate) in a hard-glass retort or flask:



The gas may be liquefied by passing it into a U-tube surrounded by ice-water, N_2O_4 collecting as a pale-yellow liquid and the oxygen escaping through a vent. The compound also is formed by the direct combination of oxygen and nitric oxide (398), and by the interaction of copper and concentrated nitric acid:



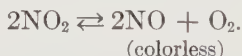
400. **Properties.** — Nitrogen tetroxide possesses a disagreeable odor and is somewhat poisonous. It may be obtained as a pale-yellow liquid which boils at 22° . At -9.4° , it forms a mass of colorless crystals. When the liquid is allowed to evaporate, it forms a reddish-brown gas, the color of which deepens as the

temperature is raised. This may be shown by carefully warming some of the substance sealed in a heavy, wide, glass tube. The increase in color is accompanied by a decrease in density, due to dissociation. At low temperatures the density corresponds with the formula N_2O_4 , and at 156° with NO_2 , a compound having one-half the molecular weight of the former. This relation can be expressed thus:



At 156° , the dissociation of nitrogen tetroxide into NO_2 is complete, while at 60.2° there are 50.04 per cent of NO_2 and 49.96 of N_2O_4 .

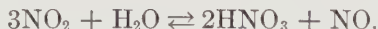
Nitrogen peroxide begins to decompose when heated above 154° , the dissociation being complete above 600° :



When nitrogen tetroxide is dissolved in cold water it functions as a double anhydride, forming a mixture of nitric and nitrous acids.



It interacts with hot water to form nitric acid and nitric oxide:

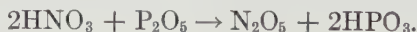


401. Nitrogen Trioxide and Nitrogen Pentoxide. — N_2O_3 is quite unstable, but it may be obtained in a more or less impure form by cooling a mixture of nitric oxide and nitrogen peroxide to a low temperature, -21° or lower:



The compound condenses to a bluish liquid. It is the anhydride of nitrous acid (393). It is usually assumed that nitrogen trioxide acts as a catalyst in the production of sulfuric acid by the chamber process, but at the temperature of the operation only NO and NO_2 could exist.

Nitrogen pentoxide can be obtained by treating anhydrous nitric acid (hydrogen nitrate) with phosphorus pentoxide, which abstracts from it the elements of water:



It may be obtained as a white crystalline solid, which decomposes between 45° and 50° . It is of no practical importance, but is interesting in that it is the anhydride of nitric acid:



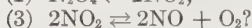
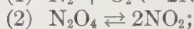
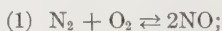
EXERCISES

1. Write down the names and formulae of the oxides and oxyacids of nitrogen, and show by equations which of the oxides are anhydrides.
2. Make an outline to show the chief possible derivatives of nitric acid.
3. Where do nitrates occur in nature? Can you explain their formation?
4. Outline three commercial methods for the manufacture of nitric acid, and point out any advantages of each of the methods. How would you prepare very pure and highly concentrated acid? What is "fuming" nitric acid?
5. State the most important chemical properties of nitric acid and illustrate fully by means of chemical equations.
6. When nitric acid is employed as an oxidizing agent, the greater the activity of the reducing agent (*i.e.*, the substance oxidized) the greater is the change in the valence of nitrogen. Explain.
7. When tin is treated with nitric acid under certain conditions, free nitrogen and stannous nitrate may be formed. Employing the electron method, write the equation.
8. When sulfur is oxidized with nitric acid under certain conditions, one of the products is nitric oxide. Write the equation.
9. Write the equation (electron method) to show the action of nitric acid upon silver.
10. Write equations to illustrate the following statement: "As a rule, the more dilute the nitric acid, the greater is the change in the valence of nitrogen."
11. What types of nitrogen compounds are powerful explosives? When a high explosive such as gun cotton or nitroglycerine breaks down, it is said to undergo "internal combustion." Explain.
12. How do smokeless powders differ in composition and action from black gunpowder?
13. What products are formed by heating the following nitrates: $\text{Ca}(\text{NO}_3)_2$, KNO_3 , NH_4NO_3 , and $\text{Hg}(\text{NO}_3)_2$?
14. Explain (including equations) how the following may be prepared: (1) an aqueous solution of nitrous acid; (2) nitrous anhydride; (3) ammonium nitrite; (4) sodium nitrite.
15. Explain fully the production of nitric oxide from the gases of the air. What difficulties are encountered? What law governs this reaction?
16. Show how nitrogen tetroxide may be prepared, and state its physical and chemical properties. Show how the following expression may be derived and explain its meaning:

$$\frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = K.$$

17. How would you distinguish a nitrate from a nitrite? nitrous oxide from oxygen?

18. What would be the effect, if any, of increased pressure upon the following equilibria:



State the law governing these changes.

19. When a mol of ammonium nitrate breaks down, what would be the total volume of the products, assuming they are measured at 409.5° and 760 mm.?

20. Why is ^aaqua regia a more powerful solvent for gold and platinum than is nitric acid?

READINGS AND REFERENCES

BRUNSWIG. Explosives.

PARTINGTON. Textbook of Inorganic Chemistry, Chap. XXIX.

REESE. Military and Industrial Explosives, Chem. in Ind., Vol. II, Chap. IX.

ROGERS. Industrial Chemistry, Chaps. V and XXVII.

CHAPTER XXIII

PHOSPHORUS AND ITS COMPOUNDS

402. **Relationships and General Characteristics.** — We have seen (Chap. XX) that phosphorus belongs to Sub-group V B, occupying the position between nitrogen and arsenic. In some respects phosphorus is closely related to nitrogen, but in other respects it is very different. Both elements are strictly acidic, and form many compounds which are analogous. Nitrogen is a colorless gas the molecules of which are diatomic (N_2) and very stable. Under ordinary conditions nitrogen is rather inert, and it requires a low temperature for its liquefaction. Its boiling point is -195.5° and its melting point -210.5° . Phosphorus, on the other hand, is a solid, which melts at 44° and boils at 287° , yielding a vapor of tetraatomic molecules (P_4). It is an exceedingly active element. Allotropic forms of phosphorus are known. Arsenic, like phosphorus, is a solid, but it has the appearance of a metal. Indeed, it is an amphoteric element. Phosphorus and arsenic form many closely related compounds, such as PH_3 and AsH_3 , PCl_3 and $AsCl_3$, P_2O_3 and As_2O_3 , P_2O_5 and As_2O_5 , H_3PO_4 and H_3AsO_4 . Nitrogen and phosphorus are two of the most important elements in plants and animals. Both nitrogen and phosphorus are much more abundant and widely diffused in nature than is arsenic. In Chapter XXXV, these elements, together with the other related elements — antimony and bismuth, — are quite fully compared.

It also is of interest to know that phosphorus closely resembles sulfur in some of its properties; but its valence is 3 or 5, while that of sulfur is 2, 4, or 6.

403. **History and Occurrence.** — It is generally supposed that phosphorus was accidentally discovered by Brand, a Hamburg alchemist and merchant, in 1669. He was searching for the philosopher's stone, hoping to be able to transmute silver into gold. Brand heated to a high temperature, in a retort, white sand and the residue from evaporated urine and observed that a vapor was formed, which condensed to a white, translucent solid having the marvelous properties of glowing in the dark and igniting spontaneously in the air. Moreover, it left a luminous trail when

drawn along a wall or board. Brand called the newly discovered substance "cold fire," owing to the fact that it was able to produce light without fire. The discovery of such a remarkable substance attracted a great deal of attention. Krafft, Kunckel (1630-1703), and Robert Boyle learned the secret of its production, but on account of the difficulty of preparation the element was almost as expensive as gold. Phosphorus was regarded as one of the wonders of nature, and Krafft made a tour of Europe, exhibiting the glowing substance before crowned heads, including Charles II of England.

The price of phosphorus remained extremely high until 1771, when Scheele, the great Swedish chemist, discovered a method for producing it from calcium phosphate, or bone-ash, which proved to be a commercial success and was employed for over a century.

Phosphorus never occurs in nature in the free state; but in the combined state it is widely disseminated, usually as phosphates, making up about 0.12 per cent of the earth's crust. The most important compound of phosphorus is *calcium phosphate*, $\text{Ca}_3(\text{PO}_4)_2$; it is the chief mineral matter found in bones. Large deposits of phosphorite occur in the United States and in North Africa. **Phosphorite** is an amorphous rock containing a large percentage of $\text{Ca}_3(\text{PO}_4)_2$. These deposits are probably of animal origin, being filled with fossil remains. In 1918, Florida marketed over 2,000,000 long tons, valued at more than \$6,000,000, which was 83 per cent of all the phosphate rock sold that year in the United States. In 1926 the United States produced 3,210,000 tons, valued at nearly \$11,000,000. Tunis exports large quantities of phosphate to Europe.

Phosphorus also occurs abundantly in the mineral **apatite**, $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2$ (or CaCl_2), which is a double salt. Extensive deposits of apatite are found in South Carolina, in the Gulf states, and in Canada. Like phosphorite, it is a source of fertilizer (super-phosphate).

Bone-ash is obtained, of course, from bones. Either the raw bones, animal charcoal, or the bones from which valuable substances have been removed by appropriate treatment are heated in the air.

Phosphorus also occurs in complex organic compounds found in living matter. Thus, it is an essential constituent of protoplasm, brain and nerve material. The element is needed to build up vegetable matter, especially the fruit and seeds of plants; consequently it is an essential constituent of certain compounds found in all fruitful soils. It is said that "phosphorus makes seeds."

The average skeleton of a man contains about 1,400 g. of phosphorus, the muscles 130 g., and the brain and nerves 12 g. There is a wide-spread popular notion that brain-activity depends to a large extent upon phosphorus. In America there has been a popular notion that "fishermen are more intelligent than farmers, because they eat so much fish, which contains so much phosphorus." The fact of the matter is that the brain contains many chemical elements and it is impossible to say that phosphorus is more important in the brain than are such elements as carbon, nitrogen, and hydrogen.

404. Preparation.—The *electric furnace process* has displaced the older method for the preparation of phosphorus. The process is electrothermic, the electricity being converted into heat.

An intimate mixture of phosphate, carbon, and silica is heated to a high temperature in an electric furnace (Fig. 136). The phosphorus is set free at the high temperature of the reaction and is distilled out of the furnace (*P*) and condensed. The sand is a flux, combining with lime (CaO) to form a slag, which is tapped off at the bottom of the furnace (*S*). The function of the carbon is to remove oxygen from the phosphorus pentoxide. The equation for the reaction may be written thus:

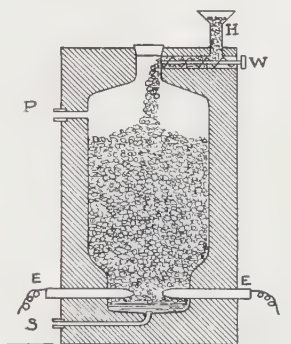
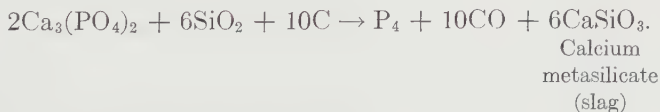
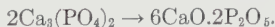


FIG. 136.



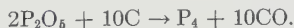
Two molecules of calcium phosphate may be regarded as containing potentially 6 molecules of lime and 2 molecules of phosphoric anhydride:



When CaO and SiO_2 unite, CaSiO_3 is formed:



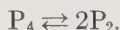
10 atoms of carbon are required to reduce 2 molecules of P_2O_5 :



The crude phosphorus which is first obtained is purified by melting under water and straining through bags made of canvas; or it may be redistilled from iron retorts. Finally, it is cast in "sticks" by pouring into glass or tin tubes surrounded by cold water.

405. Properties of Phosphorus. — Phosphorus, like sulfur, may be prepared in different forms, the two common varieties being *white (yellow) phosphorus* and *red phosphorus*.

White Phosphorus. This is the ordinary form of phosphorus, which, when slowly solidified, is transparent and almost colorless; but when quickly cooled, it is a translucent, wax-like substance. At ordinary temperatures phosphorus is soft and may be easily cut with a knife. Its sp. gr. is 1.83, its melting point 44° , and the boiling point 287° . White phosphorus is insoluble in water, but soluble in carbon disulfide, ether, turpentine, etc. From solution it crystallizes in the isometric system and is sometimes called octahedral phosphorus. This form of the element is very poisonous, less than 0.15 g. being a fatal quantity. Continued exposure to the vapor of phosphorus is likely to produce necrosis of the jawbones ("phossy jaw"). The vapor of phosphorus up to $1,500^{\circ}$ consists of tetratomic molecules (P_4), but from $1,500$ to $1,700^{\circ}$ the density of the vapor decreases, showing that dissociation occurs:



White phosphorus is a very active substance. When exposed to the air it "*phosphoresces*"; hence the name "phosphorus" (Greek, *light* + *to bear*). The luminosity of phosphorus is due to oxidation. It does not phosphoresce or oxidize in pure oxygen below 27° . The element is extremely inflammable, the kindling temperature being approximately that of the body. It must be preserved and handled under water and never touched with the hands. Phosphorus burns brilliantly in air or oxygen, forming phosphorus pentoxide, a white smoke. It may be ignited by melting under water and then passing in oxygen through a tube. Phosphorus also combines readily with the halogens, and with most metals to form *phosphides*: e.g., Ca_3P_2 .

Red Phosphorus. When white phosphorus is heated to a temperature of about 250° , air being excluded, it passes into the red form. This action can be hastened by means of a trace of iodine (catalyst). When this change occurs, heat is liberated, which means that red phosphorus contains less energy than the

white variety. Red phosphorus does not melt when heated, but it forms a vapor identical with that of white phosphorus. It has a sp. gr. of 2.25, is insoluble in carbon disulfide, and is not poisonous. As it contains much less energy than the white form, it is much less active. Red phosphorus does not catch fire in the air below 240° , so it may be safely handled. It is microcrystalline (tabular). The properties of red phosphorus are variable, indicating that it is not a pure substance.

Other modifications of phosphorus have been prepared and described. Thus, Bridgman subjected white phosphorus at 200° to a pressure of 12,000 kilos per sq. cm., and obtained a black modification having a sp. gr. of 2.691 and chemical properties similar to the red. Again, when phosphorus is crystallized from molten lead, a black form is obtained, having the appearance of a metal.

406. Uses. — The greater part of phosphorus is used in the manufacture of matches. It also is used as a poison for vermin, in the laboratory, in the preparation of bronzes, and for hardening metals. During the Great War phosphorus was employed in incendiary bombs or grenades, and was burned to make smoke screens (Fig. 137).

407. Matches. — *Friction matches* were invented by John Walker, of England, in 1827. The head of the match contained potassium chlorate, antimony trisulfide, and glue. They were ignited by drawing them through two layers of sand-paper. Phosphorus was soon substituted for antimony trisulfide. Sulfur was used for coating the matches, but wax or paraffin was found to be more agreeable, owing to the sharp odor of sulfur dioxide. Potassium nitrate may be used in place of potassium chlorate. Owing to the poisonous effect of phosphorus upon the workmen, one nation after another has forbidden the use of white phosphorus in the manufacture of matches. In 1913, our Government placed a tax of two cents per hundred on the manufacture of matches by the old process. Fortunately there is a sulfide of phosphorus (P_4S_3) which is cheap and does not produce necrosis; it is now used in the head of the ordinary match.

“Safety” (Swedish) matches were invented by Böttger in 1848. Neither phosphorus nor a compound of phosphorus is used in the head of the safety match, but it consists of an oxidizing agent (Pb_3O_4 , $KClO_3$, $K_2Cr_2O_7$), antimony trisulfide, powdered glass and glue (or dextrin). These matches are ignited by rubbing them on a surface consisting of antimony trisulfide, red phosphorus,

and glue. If the so-called safety match be dry and drawn quickly over glass, slate, etc., it can be ignited.

In general, the head of a match contains an oxidizing agent and a combustible material. When rubbed on a rough surface, heat is generated by friction, and the combustible material is raised to its kindling temperature.



Courtesy of C. W. S., War Department.

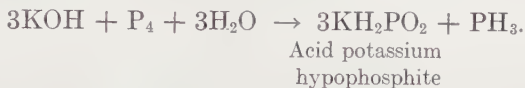
FIG. 137. Burst of Phosphorus Airplane Drop Bombs.

The white cloud of phosphorus pentoxide (P_2O_5), produced by the burning phosphorus, envelops the ship.

The manufacture of matches is an interesting process. Blocks of white pine are fed into a machine and cut into sticks, which are forced into holes of metal plates. The plates are then fastened together in the form of an endless chain, followed by treatment with appropriate materials for completing the matches. The manufacture of matches, from wood to finished product, is all done by machinery.

COMPOUNDS OF PHOSPHORUS

408. **Phosphine, PH_3 .** — *Hydrogen phosphide* or *phosphine*, PH_3 , may be prepared by heating white phosphorus with a concentrated solution of potassium hydroxide:



The gas thus prepared is not pure, but is mixed with a small amount of P_2H_4 , which is a liquid and spontaneously inflammable. Phosphine can be formed by introducing a little white phosphorus into a flask containing a solution of caustic potash (Fig. 138). Hydrogen or illuminating gas is then passed into the flask in order to displace all the oxygen so that an explosion may not occur. The flask is now carefully heated, and as bubbles of hydrogen phosphide come in contact with the air, they ignite spontaneously and burn, forming smoke rings of phosphoric acid:

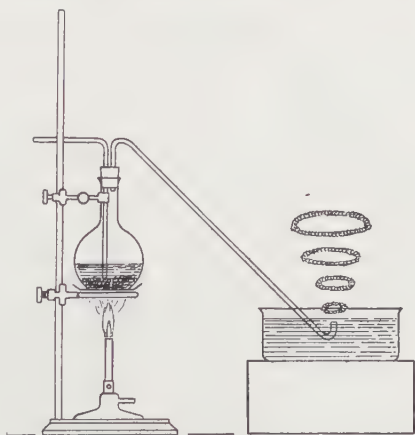
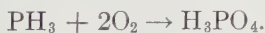


FIG. 138.

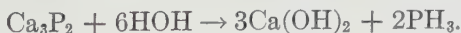


Phosphine is a colorless, poisonous gas with a disagreeable odor, like that of rotten fish. It is analogous to ammonia, but is less strongly basic. Thus, it combines with HI to form *phosphonium iodide*, a compound somewhat similar to ammonium iodide and ammonium chloride:



PH_4I dissociates at a lower temperature than does NH_4Cl . The phosphonium-ion, PH_4^+ , is unstable.

Phosphine also can be prepared by the *hydrolysis of phosphides*:



This reaction is similar to the hydrolysis of nitrides to form ammonia:



When phosphine is carefully purified, it is not spontaneously inflammable.

409. **Halides of Phosphorus.** — White phosphorus burns in dry chlorine gas, forming **phosphorus trichloride**, PCl_3 ; or, when chlorine is in excess, **phosphorus pentachloride**, PCl_5 . Phosphorus trichloride is a colorless, fuming liquid with a very sharp odor, boiling at 76° . The compound is readily hydrolyzed, with the formation of hydrochloric and phosphorous acids:

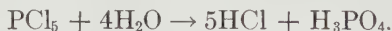


All the halides of phosphorus undergo complete hydrolysis with excess of water.

Phosphorus pentachloride is a whitish or yellowish-white crystalline substance, which possesses a sharp odor. When exposed to moist air it interacts with water to form **phosphorus oxychloride** (phosphoryl chloride):



When treated with excess of water, it dissolves with evolution of heat, forming hydrochloric and phosphoric acids:



When phosphorus pentachloride is heated it *dissociates*, the dissociation being practically complete above 300° :



Other halides of phosphorus are known. PF_3 and PF_5 are gases, PBr_3 is a liquid, and PBr_5 and PI_3 are solids. PBr_5 , like PCl_5 , dissociates when heated:



For the condition of equilibrium we have (214)

$$\frac{[\text{PBr}_3] \times [\text{Br}_2]}{[\text{PBr}_5]} = K.$$

Since PBr_5 and PBr_3 are colorless and Br_2 is reddish-brown, this reaction may be employed to show the effect of change of concen-

tration of a reactant upon a system in equilibrium. This may be illustrated by the following *experiment*:

Equal quantities of PBr_3 are introduced into two glass tubes of the same volume, a small quantity of PBr_3 is added to the second tube, and both tubes are then tightly sealed up. When the tubes are heated to the same temperature, the contents of the first tube will be more deeply colored than those of the second tube (explain).

410. **Oxides of Phosphorus.** — Phosphorus forms three oxides:

Phosphorus trioxide or phosphorous anhydride.....	$\text{P}_2\text{O}_3(\text{P}_4\text{O}_6)$
Phosphorus tetroxide.....	P_2O_4
Phosphorus pentoxide or phosphoric anhydride.....	$\text{P}_2\text{O}_5(\text{P}_4\text{O}_{10})$

The vapor densities of the first and third of these oxides show that their molecular formulae are P_4O_6 and P_4O_{10} , but for the sake of simplicity in writing chemical equations P_2O_3 and P_2O_5 will be used.

Phosphorus trioxide can be prepared as a wax-like mass or as feathery crystals by the slow oxidation of phosphorus. It has the odor of phosphorus and is poisonous. This oxide melts at 22.5° and boils at 173° . The oxide dissolves slowly in cold water to form phosphorous acid; but with hot water a violent, complicated reaction takes place. When phosphorous oxide is heated to 440° it decomposes, yielding phosphorus tetroxide (P_2O_4) and red phosphorus.

Phosphorus pentoxide is readily obtained in the form of dense white clouds by burning phosphorus in excess of dry air or oxygen. The fumes may be easily condensed upon the sides of a cold vessel. The oxide may be obtained as a white flocculent powder or in the form of a glassy mass. Phosphorus pentoxide has great affinity for water, and on account of this property it is one of the best dehydrating agents known. P_2O_5 dissolves in cold water to form metaphosphoric acid (HPO_3), and in hot water to form orthophosphoric acid (H_3PO_4). The vapor density of phosphoric anhydride at $1,400^\circ$ corresponds with the formula P_4O_{10} .

411. **Oxyacids of Phosphorus.** — The most common oxyacids of phosphorus are the following:

Orthophosphoric acid.....	H_3PO_4	} (anhydride, P_2O_5)
Pyrophosphoric acid.....	$\text{H}_4\text{P}_2\text{O}_7$	
Metaphosphoric acid.....	HPO_3	
Hypophosphoric acid.....	H_2PO_3	(anhydride, P_2O_4)
Phosphorous acid.....	H_3PO_3	(anhydride, P_2O_3)
Hypophosphorous acid.....	H_3PO_2	(no anhydride known)

We have seen that halides of phosphorus undergo hydrolysis when treated with water (298). These reactions are of importance in establishing the constitution of certain of the acids of phosphorus.

Orthophosphoric acid is the most important acid containing phosphorus.

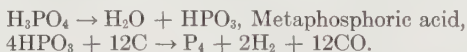
412. **Orthophosphoric Acid, H_3PO_4 .** — *Orthophosphoric acid*, commonly called *phosphoric acid*, can be prepared by a number of different methods:

(1) *By treating bone-ash or natural phosphate with sulfuric acid:*



Calcium sulfate is eliminated by filtration or by decantation, and phosphoric acid obtained by evaporation of the solution.

Before the invention of the electrothermic process for the production of phosphorus, the reaction shown by the above equation was the first one carried out in the preparation of phosphorus. The acid was evaporated to a syrup, mixed with charcoal, and then heated:



(2) *By oxidizing red phosphorus with nitric acid:*



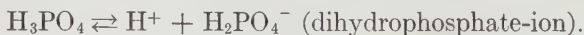
The excess of acid is removed by evaporation and the process repeated until oxidation is complete.

(3) *By treating phosphorus pentoxide with hot water:*



Phosphoric acid (hydrogen phosphate) is a white, deliquescent solid and extremely soluble in water, to which it imparts a pleasant purely acid taste. The concentrated solution is a thick syrup.

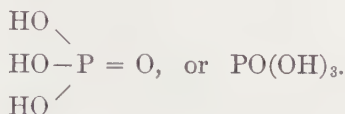
In aqueous solution it is much weaker than sulfuric acid, and it is tribasic (242). H_3PO_4 dissociates primarily thus:



In dilute solution the dihydrophosphate-ion has some tendency to dissociate:



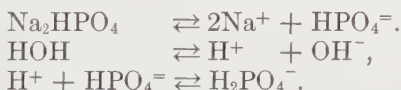
The formation and properties of phosphoric acid (formation by hydrolysis of PCl_5 , basicity, etc.) can best be explained by writing its graphic formula thus:



413. Phosphates. — Since phosphoric acid is tribasic it forms three classes of salts:

$\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$,	Sodium dihydrogen phosphate (<i>primary salt</i>)	} Acid Salts
$\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$,	Disodium hydrogen phosphate (<i>secondary salt</i>)	
$\text{Na}_3\text{PO}_4 \cdot 2\text{H}_2\text{O}$,	Sodium phosphate (<i>tertiary salt</i>).	

The phosphates of sodium and of potassium are soluble in water. An aqueous solution of NaH_2PO_4 is faintly acid (why?). A solution of Na_2HPO_4 is slightly alkaline, due to hydrolysis, which produces hydroxide-ion:



Hydrogen-ion (from water) combines with $\text{HPO}_4^=$ to form H_2PO_4^- , leaving hydroxide-ion. In other words, some sodium hydroxide is formed.

An aqueous solution of Na_3PO_4 is strongly alkaline (why?). It is obtained by treating a solution containing a mol of the secondary salt with a mol of sodium hydroxide, followed by evaporating the solution to dryness:



Sodium ammonium hydrogen phosphate, or **microcosmic salt**, $\text{NaNH}_4\text{HPO}_4 \cdot 4\text{H}_2\text{O}$, is a white crystalline compound, which is excreted in the urine; it is a mixed salt (249).

The **phosphates of calcium** are as follows:

$\text{CaH}_4(\text{PO}_4)_2$,	Primary calcium phosphate;
$\text{Ca}_2\text{H}_2(\text{PO}_4)_2$,	Secondary calcium phosphate;
$\text{Ca}_3(\text{PO}_4)_2$,	Tertiary calcium phosphate.

The primary salt is soluble in water and is used extensively as fertilizer (superphosphate). The tertiary phosphate is insoluble,

and to make it available as plant food it is treated with dilute sulfuric acid:



This mixture of primary calcium phosphate and gypsum is sold under the name of "superphosphate of lime," and is used on an enormous scale as a fertilizer.

As previously stated, phosphates are obtained chiefly from phosphate rock, bones, and the mineral apatite. These phosphates are practically insoluble in water, but about 1840 Sir John Laws discovered that when they are treated with sulfuric acid, the product is much more effective in the growth of plants than is the untreated material. About 45 per cent of our output of sulfuric acid is used in the production of fertilizers, including superphosphate of lime and ammonium phosphate.

When farm products are sold, phosphorus is gradually removed from the soil; to make good the loss it is necessary to supply fertilizer in the form of phosphates. According to T. M. Lowry, the pasture lands of England became greatly impoverished a century ago, on account of the removal of phosphorus; but the fertility of the soil was restored by manuring it with bones gathered from the battlefields of Europe. In this connection it is of interest to note that the growth of the indigo-plant is largely dependent upon phosphates.

The world's consumption of phosphate rock is ordinarily about 5,000,000 tons annually.

When a solution of a phosphate is treated with one of silver nitrate, a *yellow precipitate of silver phosphate* is obtained:



As phosphates are soluble in strong acids, it is necessary to neutralize HNO_3 to secure complete precipitation.

Ammoniacal solutions of phosphates yield a white crystalline precipitate when treated with a solution of a magnesium salt:



The salt crystallizes with six molecules of water —

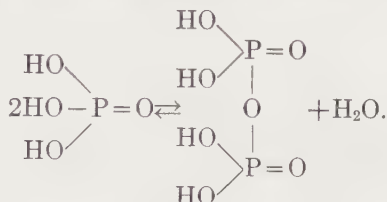


It is an important phosphate of magnesium, being used in quantitative analysis for estimating both magnesium and phosphoric acid. This reaction is carried out in the presence of ammonium chloride.

414. **Pyrophosphoric Acid, $\text{H}_4\text{P}_2\text{O}_7$.** — This compound can be obtained by heating H_3PO_4 to 200° to 300° :



Graphically, the change may be represented thus:



Pyrophosphoric acid is a colorless glassy mass, which melts at about 61° ; it is soluble in water, with which it unites to form H_3PO_4 . *Pyrophosphates may be prepared by heating secondary phosphates:*



Ammonium magnesium phosphate, when heated, yields *magnesium pyrophosphate*, a very stable salt:



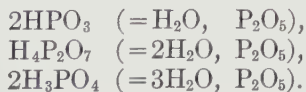
415. **Metaphosphoric Acid, HPO_3 .** — Metaphosphoric acid can be obtained by heating orthophosphoric acid to a high temperature:



It also may be formed by dissolving P_2O_5 in cold water:



It should be noted in this connection that P_2O_5 is the anhydride of the three acids of phosphorus which we have studied; it is simply a matter of hydration. Phosphoric acid is formed when P_2O_5 is thoroughly hydrated. The degrees of hydration of the anhydride may be shown as follows:



Metaphosphoric acid is prepared in the form of white, deliquescent sticks (the "glacial phosphoric acid" of commerce). It is soluble in cold water with which it combines ultimately to form phosphoric acid. By boiling the solution, H_3PO_4 is formed quickly.

Metaphosphates can be obtained by heating primary orthophosphates:



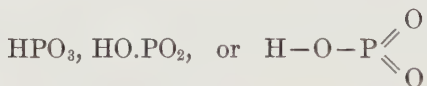
When microcosmic salt is heated to a high temperature, *sodium metaphosphate* is formed:



This salt is used by chemists and mineralogists as a test for certain metallic oxides. A bead is prepared by heating a little microcosmic salt on the end of a platinum wire. When minute quantities of certain metallic oxides are heated in contact with the beads in the flame of a burner, characteristic colors are obtained. Thus, cobalt oxide colors the bead blue:



The structure of metaphosphoric acid is similar to that of nitric acid:



Metaphosphoric acid coagulates albumin (white of egg suspended in water), while ortho- and pyrophosphoric acid do not.

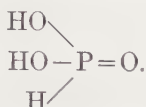
Hypophosphates, salts of hypophosphoric acid, are known: e.g., Na_2PO_3 and NaHPO_3 . The acid can be obtained from its salts, but it is of minor importance.

416. Phosphorous Acids. — *Phosphorous acid*, H_3PO_3 , can be prepared by the hydrolysis of phosphorus trichloride. The acid also is formed when phosphorus trioxide is dissolved in cold water:

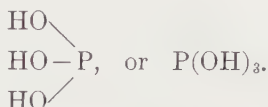


Phosphorous acid is a crystalline solid which melts at 70.1° ; it is a *powerful reducing agent*, and a weak tribasic acid. Ordinarily, however, only two of its hydrogen atoms are replaceable

by metals, which indicates that the constitution of the compound is



Its formation by the hydrolysis of PCl_3 indicates, on the other hand, that its graphic formula is



When phosphorous acid is strongly heated, it forms metaphosphoric acid and phosphine:



The salts of this acid are called **phosphites**.

Hypophosphites are salts of *hypophosphorous acid*. These compounds can be obtained by boiling phosphorus with a solution of an alkali (408):



Hypophosphorous acid and hypophosphites are reducing agents. Thus, their aqueous solutions precipitate silver and gold from their solutions.

. 417. **Sulfides of Phosphorus.** — Phosphorus forms several sulfides, among which are P_2S_3 , P_2S_5 , and P_4S_3 . Phosphorus pentasulfide is used in organic chemistry for replacing oxygen with sulfur. It may be prepared by heating red phosphorus and sulfur with carbon disulfide, fine, pale-yellow crystals separating out. Phosphorus sesquisulfide, P_4S_3 is used in the manufacture of "non-poisonous" matches (407).

EXERCISES

1. Show the relation of phosphorus to nitrogen.
2. Give the history, the occurrence, and the preparation of phosphorus. How can red phosphorus be prepared from white phosphorus? State the physical and the chemical properties of these two forms of phosphorus. Write all chemical equations involved.
3. Explain the meaning of the following terms: phosphorescence; luminescence (animal); incandescence; and fluorescence.

4. How may phosphine be prepared? Give its properties, and show its resemblance to ammonia.

5. Outline the chemistry of the most important halides of phosphorus. Explain the effect of water upon PBr_3 and PBr_5 .

6. When ethyl alcohol ($\text{C}_2\text{H}_5\text{OH}$) is poured upon PCl_5 , ethyl chloride, phosphoryl chloride (POCl_3), and hydrogen chloride are formed. Write the equation. The addition of PCl_5 to such compounds as the alcohols (752) shows the presence of what group or radical?

7. Outline the preparation and the properties of the principal oxides and acids of phosphorus.

8. Show that phosphoric acid is tribasic, and explain the action upon litmus of aqueous solutions of its potassium salts.

9. What is "superphosphate of lime" and how is it manufactured? Tertiary calcium phosphate is practically insoluble in water. When farmers turn under phosphate rock by plowing they find that in the course of time it becomes available, in part, as plant-food. Explain.

10. What are formed when the following substances are heated: $\text{NaNH}_4\text{HPO}_4$, K_2HPO_4 , KH_2PO_4 , H_3PO_4 , and $\text{H}_4\text{P}_2\text{O}_7$?

11. How could you differentiate the following acids from each other: phosphoric, pyrophosphoric, and metaphosphoric?

12. When microcosmic salt is used as a test for a metallic oxide such as CuO , what chemical changes take place? Write equation.

13. Why is phosphorous acid a powerful reducing agent?

14. What weight of phosphorus could be prepared from 1,000 kilograms of a rock containing 95 per cent of calcium phosphate?

15. One-hundredth of a mol of phosphorus pentachloride is dissolved in water contained in a tightly stoppered vessel, and the solution then diluted exactly to four liters. How much replaceable (acid) hydrogen does one liter of the solution contain? What is its normality?

16. Compare and contrast the properties of phosphorus and sulfur.

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CHAPTER XXIV

CARBON. C = 12

418. **Relationships and General Characteristics.** — Carbon belongs to Group IV (81), being closely related to silicon. This group may be regarded as a transition group which links the more electropositive elements of Groups I, II, and III with the more electronegative elements of Groups V, VI, and VII.

Carbon and silicon are strictly non-metals in their chemical properties, differing markedly from the common metals tin and lead, which also belong to Group IV. These elements possess a maximum valence of 4, forming halides of the type MX_4 , hydrides MH_4 , and oxides RO_2 .

Carbon and silicon exhibit well-defined allotropy, one allotropic form at least of which is hard and crystalline and has a pronounced luster. They possess high melting points, and in the amorphous state are poor conductors of heat and electricity. While carbon occurs in the free state, silicon always occurs in combination, being exceedingly abundant. Silicon unites directly with chlorine at 450° and with bromine at 500° ; but carbon unites directly with only one of the halogens, namely, fluorine (CF_4). The elements unite to form silicon carbide (SiC), an exceedingly hard substance. Each element combines directly with oxygen to form a feeble acid anhydride. They form a large number of analogous compounds. Some of their properties and characteristics are summarized in the table below.

CARBON AND SILICON

Element	At. Wt.	At. No.	M.P.	Analogous Compounds				
Carbon, C..	12.00	6	above $3,500^\circ$	CO_2	CH_4	CCl_4	$CHCl_3$	$CaCO_3$
Silicon, Si..	28.06	14	$1,420^\circ$	SiO_2	SiH_4	$SiCl_4$	$SiHCl_3$	$CaSiO_3$

As compared with atoms of carbon, the atoms of silicon have but little tendency to unite to form chain compounds (450).

419. **Occurrence of Carbon.** — *Carbon* (Latin *carbo*, coal or charcoal) occurs in the free state in the form of the diamond and

graphite. Carbon is a constituent of animal and vegetable tissues and of coal, petroleum, and natural gas. It may be regarded as the central element of the Organic Kingdom. Moreover, carbon is a constituent of all alcohols, animal and vegetable oils and fats, sugars, cellulose, ethers, etc. In combination with oxygen, it occurs in carbon dioxide, and very abundantly in carbonates, such as calcium carbonate (chalk, marble, and limestone) and magnesium carbonate. Carbon compounds are exceedingly numerous, over 230,000 being known.

Not only is carbon closely related to life, but to energy as well; for by the oxidation of the element most of the energy of our bodies and for carrying on the work of the world is produced.

While carbon is widely distributed in the earth's crust, it is only a minor constituent of it, — about 0.2 per cent of the outer 10 miles.

THE DIAMOND

420. **Occurrence.** — The diamond has been used for ages as a precious stone. Originally it was obtained solely from alluvial deposits in India. Since the year 1727 the rich diamond fields of Brazil have been worked. In 1867 diamonds were discovered in South Africa, and the most famous mines in the world are the Kimberley, De Beers, etc. Diamonds are also found in Australia, in the Ural, and in other localities. They also have been found in meteorites. The diamonds of South Africa occur in great pipes extending vertically downward to unknown depths. These pipes are filled with a heterogeneous mixture, cemented with a bluish hard material, in which "blue earth" the diamonds are imbedded. About 10 million parts of "blue earth" contain 1 part of crystalline carbon. The origin of the diamond has always been a riddle, but it must have been formed at vast depths under very great pressure and at high temperature. There is evidence to show that diamonds have crystallized out from a lava or magma which consists largely of magnesium silicates.

The history of some of the large diamonds is most interesting. The largest diamond ever found was the celebrated "Cullinan"; it was discovered in South Africa in 1905, and weighed in the rough state 3,032 carats (1.37 pounds avoirdupois). It was presented to King Edward the VIIth. This diamond was cut into a number of stones, the largest of which weighed 516.5 carats. The Orloff diamond was stolen by a French soldier from the eye of an idol in a Brahman temple, and subsequently stolen from him by a ship's captain. Finally, it was bought by Prince Orloff for £90,000, and presented to Empress

Catherine II of Russia. It weighs 194 $\frac{3}{4}$ carats, and is tinged with yellow. The Pitt or Regent diamond is a magnificent colorless diamond which weighs 136 $\frac{1}{4}$ carats. It is in the Louvre (Paris). This stone was found by an Indian slave, who wandered to Madras, where he was murdered on board a ship, and the diamond sold for £1,000. In 1710 it was purchased by Thomas Pitt, grandfather of the Earl of Chatham, for £10,000; and in 1717 he sold it to the Duke of Orleans for £130,000. The Kohinoor diamond, one of the British crown jewels, weighs 106 carats. Its authentic history begins before the birth of Christ. The celebrated Hope diamond weighs 44 $\frac{1}{4}$ carats and has an exquisite blue color. The Tiffany diamond weighs 125 $\frac{1}{2}$ carats and has a magnificent orange-yellow color. The Victoria, a diamond of 180 carats, was cut from a stone weighing 457 $\frac{1}{2}$ carats and sold to the Nizam of Hyderabad for £400,000, which was at the rate of \$20,000,000 per pound troy.

421. **Artificial Diamonds.** — Moissan (1893) first prepared artificial diamonds. Pure sugar charcoal (carbon) was packed in a graphite crucible with pure iron, the crucible placed in an elec-

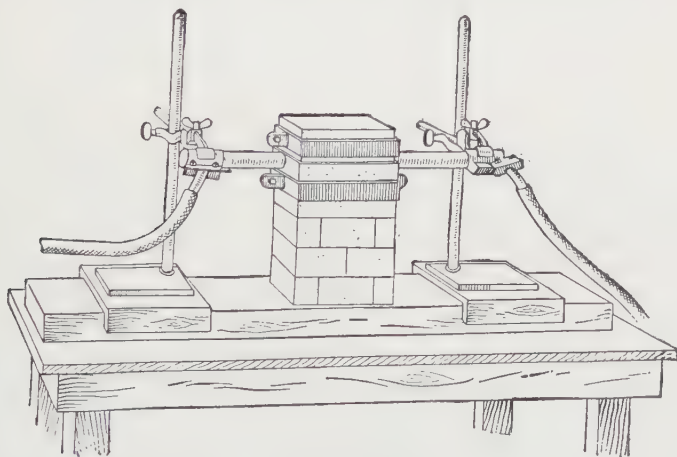


FIG. 139. Moissan's Electric Furnace.

tric furnace (Fig. 139), and a powerful arc formed between carbon electrodes. The temperature rose to 3,000° to 4,000° C., and carbon dissolved in the molten iron. The fiery crucible was then plunged into cold water and cooled, and the carbon in the inner part of the vessel was subjected to an enormous pressure. The metal was dissolved in acids, and the residue treated with appropriate reagents and then washed; it consisted chiefly of graphite, but exceedingly small diamonds were also present, some of which

were colorless and others black. These diamonds possessed all the properties of the natural diamond.

422. Properties. — The diamond crystallizes in the isometric (regular) system. When the diamond is examined by means of X-rays (64) it is found to consist of atoms arranged as shown in Fig. 29. The carbon atoms are arranged in the form of tetrahedra, with four atoms at each corner and a fifth atom at the mass-center. The average sp. gr. is about 3.5, and it is the hardest substance known. It has a high index of refraction, and its property of scattering light to such a great extent renders it very valuable as a gem. The pure diamond is colorless and transparent, but is frequently colored by small quantities of impurities. Some of the blue, red, or green stones are as valuable as the colorless variety. The black variety (*carbonado* or *bort*) is of no value as a gem, but on account of its extreme hardness it is used for boring, cutting, and grinding. The diamond is very resistant to the action of most chemicals; it is not attacked by acids. When it is heated in the absence of air above $1,000^{\circ}$, it is transformed into a coke-like mass. When heated in air or oxygen to a high temperature, it burns to form carbon dioxide (Lavoisier, 1772). Davy (1814) proved that carbon dioxide is the sole product formed (excepting a very small amount of ash) when the diamond is burned. Before use as a jewel, the diamond is cut. The greater part of the diamond cutting is done in Holland. The new international carat is 0.2 g.

GRAPHITE

423. Occurrence. — *Graphite* (Greek, meaning *write*) was known to the ancients, but originally it was confused with the sulfide of molybdenum (MoS_2); hence both minerals were termed *plumbago*. Graphite is distributed widely in nature, being found in Ceylon, Madagascar, Korea, the United States, Canada, Mexico, Europe, etc. Graphite commonly occurs in lumps or nodules in the old crystalline rocks, such as granite and gneiss. It occurs in nature in two forms — crystalline and “amorphous.”¹ In 1918 the United States produced about 6,000 tons of each of these varieties. The crystalline form is far more valuable.

424. Preparation of Graphite. — Graphite is manufactured on a large scale by the **Acheson process**, chiefly at Niagara Falls, where water power is transformed into electricity. Amorphous

¹ Amorphous is used here in a trade sense. As a matter of fact, this form of graphite consists of fine crystals.

carbon (anthracite coal or coke) is heated in an electric furnace in the presence of ferric oxide or silica, which acts as a catalyst in the formation of graphite. A carbon rod (*C*) is used as a core between the terminals (Fig. 140). Carbides are first formed, but at the very high temperature attained ($3,500^{\circ}\text{C.}$) these dissociate, yielding graphite, which is deposited as nearly pure carbon. The electrodes (*A*) are made of graphite. The furnace is nearly filled with coarse grains of anthracite coal or coke (*B*). The charge is covered with a mixture of sand and carbon (*D*). Graphite also is formed when melted iron containing carbon in solution cools (683).

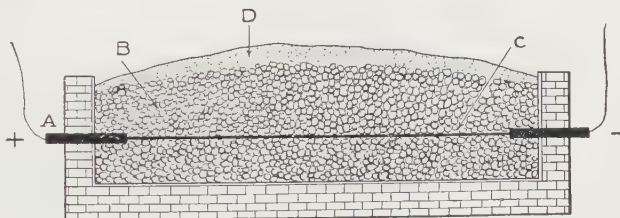


FIG. 140.

425. Properties. — Graphite is a soft, gray-black, shiny substance which feels greasy to the touch. Its density is about 2.2, and, unlike the diamond, it is a good conductor of heat and electricity. Graphite leaves a black mark when drawn across paper. It formerly was supposed to contain lead, hence the name black-lead or plumbago. Not many chemical reagents attack graphite appreciably. Even oxygen at a high temperature does not attack it readily.

The arrangement of the atoms of carbon in graphite is in the form of a hexagonal network, being quite different from that of the diamond.

426. Uses. — Graphite, mixed with fireclay, is used very extensively in the manufacture of crucibles, which are very resistant to heat and chemical action. The graphite should be of a high degree of purity. Amorphous graphite and graphite dust from flake graphite are used on a large scale for foundry facings. The demand for graphite as a lubricant appears to be constantly increasing. A mixture of graphite and clay is used in the manufacture of "lead" pencils. It also is used in painting iron, for fillers of dry cells, electrotypers' leads, stove and metal polish, glazing powder, polishing shot, etc. Artificial graphite can be

used for practically any purpose to which natural graphite is put. It is particularly adapted to the manufacture of electrodes, and is largely utilized also in the manufacture of lubricants, paints, etc.

"AMORPHOUS" CARBON

427. **Charcoal.** — The purest "amorphous" carbon is made by heating cane sugar, air being excluded:



The charcoal is freed from mineral matter by boiling with acids, and is then ignited in a current of chlorine to remove the last traces of hydrogen. Moissan used sugar charcoal in the preparation of diamonds. Charcoal is manufactured on a very large

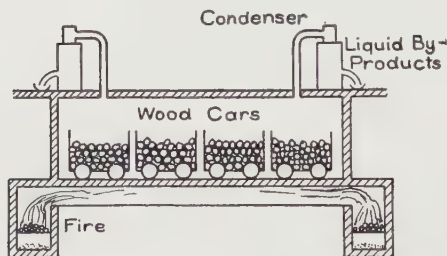


FIG. 141.

scale by heating wood in retorts; that is, the vegetable matter is subjected to destructive distillation (Fig. 141). Various volatile by-products, such as wood (methyl) alcohol, acetone, and acetic acid are obtained.

Boneblack, or *animal charcoal*, is manufactured by heating bones and animal refuse in iron retorts. The volatile matter (bone oil) is driven off and condensed, and the residue consists of mineral matter — chiefly $\text{Ca}_3(\text{PO}_4)_2$ — and a relatively small amount of carbon. The calcium phosphate can be dissolved by treating the boneblack with hydrochloric acid, but for most purposes this is not necessary. Boneblack possesses much greater decolorizing and adsorbing power than does vegetable charcoal. It is used on a large scale for the purification of sugar.

Coke is produced on an enormous scale by subjecting soft coal to destructive distillation, or carbonization. The *by-product oven* is a brick chamber surrounded by heating-flues and furnished with a pipe through which the volatile products may be led off. When the retort or by-product oven is employed, most valuable by-products are obtained, such as gas, coal-tar, and ammonia. Before the war the greater part of coke in the United States was

produced in the wasteful beehive oven; but by 1924 we were producing 70 per cent of it in the by-product oven. The increased use of the by-product oven is an important conservation measure. According to F. W. Sperr, Jr., *the following products are obtained from one ton of Pittsburgh coal*:

Total coke.....	1,500 pounds
Gas.....	11,360 cubic feet
Tar.....	12.4 gallons
Ammonium sulfate.....	24 pounds
Light oil (benzenes).....	4 gallons

About sixty million tons of coke are produced annually in the United States. It is used largely for removing oxygen from metals and as a source of heat.

Lampblack, a form of soot, is manufactured by the incomplete combustion of organic substances, usually of an oily or of a resinous character, the carbon depositing as soot in a series of chambers. It often deposits on a lamp chimney when the draft is not properly regulated. Lampblack is used in the production of printer's ink, in the preparation of black paint, and in calico printing.

Carbon-black or *gas-black* is produced by allowing a flame, when the gas is burning in an insufficient supply of air, to impinge upon a cold surface, such as a revolving iron drum. It is used in the manufacture of printer's ink and automobile tires. It adds much to the length of life of tires. The United States produced nearly 200,000,000 pounds of carbon-black in 1927, valued at about 11 million dollars.

Gas-carbon is formed in the manufacture of coal gas, being found as a deposit in the upper portion of the retort; it is a very hard iron-gray mass. Gas-carbon is a good conductor of electricity and is therefore used in the manufacture of electrodes.

Coal is formed by slow changes in vegetable matter. When such matter decays out of contact with air (*e.g.*, under water or when covered with sand or clay), water and hydrocarbons and other products escape and a residue richer in carbon is left. Anthracite coal is the richest in carbon, for it has undergone the greatest change; bituminous coal contains less carbon; and lignite and peat are imperfectly formed coals, being more nearly like wood in composition. This is clearly shown in the table given below.

	Carbon	Hydrogen	Oxygen and Nitrogen
Wood (Cellulose).....	51	6	43
Peat.....	58	6	36
Lignite.....	70	5	25
Bituminous coal.....	81	5	..
Anthracite.....	94	3	..

The wood, peat, and lignite, as given in the table, are free of water and ash. The percentages of carbon in the same variety of coal vary considerably.

In 1918, the United States produced 579,385,820 tons of bituminous coal and 98,826,084 tons of Pennsylvania anthracite.

428. Physical Properties of Charcoal. — Charcoal is practically infusible. At the temperature of the electric furnace ($3,500^{\circ}\text{C.}$), it is partly volatile. Charcoal is very porous and has the property of being able to take up large volumes of gases and vapors; it also takes up certain coloring matters. This phenomenon is known as **adsorption**, and may be strikingly illustrated by introducing a piece of freshly ignited charcoal into an inverted glass tube containing ammonia gas confined over mercury. The charcoal adsorbs many times its volume (as much as 90 in the case of boxwood charcoal) of the gas, and mercury rises in the tube. Since charcoal is very porous, it exposes a large surface to the gas, the molecules of which are apparently concentrated or held upon the surface of the carbon. According to J. Hunter, one cc. of charcoal absorbs (S.T.P.) 171.7 cc. of ammonia, 86.3 cc. of nitrous oxide, 67.7 cc. of carbon monoxide, 21.2 cc. of carbon dioxide, 17.9 cc. of oxygen, 15.2 cc. of nitrogen, and 4.4 cc. of hydrogen.

When a solution of indigo is filtered through a column of bone-black, the coloring matter is removed. This material, as stated before, is utilized in the purification of sugar.

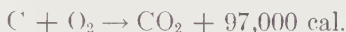
The average density of wood charcoal is about 1.5, but it floats in water owing to the fact that it contains adsorbed air. Charcoal is a good deodorizer and decolorizer.

X-ray analysis has shown that charcoal is more or less crystalline, the arrangement of the atoms being like that in graphitic carbon, which consists of a hexagonal network of carbon atoms.

It should be added that charcoal differs considerably in its properties, depending upon the variety of wood from which it is produced, as well as upon the process employed in its manufacture.

Charcoal for gas masks is prepared from coconut or other shells, and it has been found that its activity is greatly increased by reheating the charcoal in steam or air. It is introduced into canisters and is an excellent adsorbent for toxic gases or vapors, such as phosgene. According to A. D. Little, specially prepared or activated charcoal may have an internal area as great as twenty thousand square yards, or about four acres, per cubic inch.

429. **Chemical Properties of Carbon.** — At ordinary temperatures carbon is not a reactive substance. Graphite appears to be the most stable form, for at very high temperatures other forms of carbon are changed to graphite (424). When carbon is heated in air or oxygen it burns to form carbon dioxide with the liberation of energy:



In a limited supply of oxygen, carbon monoxide is also formed. At high temperatures it combines with sulfur to form carbon disulfide (CS_2), with silicon and with certain metals to form **carbides**: *e.g.*, SiC , CaC_2 and Al_4C_3 . M. Berthelot showed that carbon unites directly with hydrogen to form acetylene (C_2H_2) when an electric arc is passed between carbon poles surrounded by hydrogen. It also combines with iron to form a carbide (Fe_3C).

Carbon, at high temperatures, is an excellent reducing agent. Enormous quantities of it are used in metallurgical operations, such as the reduction of oxides of iron and of zinc.

CARBON DIOXIDE, CO_2

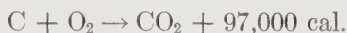
430. **History.** — van Helmont, in the seventeenth century, was the first to distinguish between carbon dioxide and ordinary air. He called it *gas sylvestre*, and obtained it by different methods. Joseph Black (1754) showed that carbon dioxide could be obtained by heating such compounds as the carbonates of calcium and magnesium, and that it was absorbed by alkalis; hence it was called by him "fixed air." Black's investigation of *magnesia alba* (MgCO_3) was of fundamental importance. Among other things, he proved that magnesium carbonate yields, when heated, carbon dioxide and magnesium oxide (*magnesia usta*); also that it effervesces when treated with vitriolic acid (H_2SO_4), forming Epsom salt. He clearly showed that the difference between *magnesia*

alba (MgCO_3) and *magnesia usta* (MgO) was the gas "fixed air," i.e., carbon dioxide.

Lavoisier first properly explained the chemical nature of the gas by burning carbon in oxygen obtained from mercuric oxide.

431. Occurrence and Sources. — Carbon dioxide occurs in the air, in natural waters, and in the soil; it escapes through vents and fissures in the earth's crust in certain localities: e.g., the Poison Valley in Java and the *Grotta del Cane* near Naples. According to Mendeléeff, there is a depression near the Rhine, in the neighborhood of extinct volcanoes, which is constantly filled with carbon dioxide. "The insects which fly to this place perish . . . The birds chasing the insects also die, and this is turned to profit by the local peasantry." The carbon dioxide found in nature comes from a number of different sources, such as combustion, decay, fermentation, respiration, and the decomposition of carbonates. Vast quantities of the carbonate of calcium (limestone, marble, chalk, etc.) and of magnesium carbonate also occur in nature. *Dolomite* is magnesian limestone ($\text{CaCO}_3 \cdot \text{MgCO}_3$). Other carbonates such as *siderite* (FeCO_3), *smithsonite* (ZnCO_3), and *withelite* (BaCO_3) are fairly abundant.

432. Formation. — (1) *Carbon dioxide is formed when carbon or matter containing carbon is burned:*

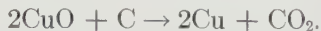


The same chemical change also occurs, during respiration, in the bodies of animals; also when vegetable and animal matters decay.

(2) *By the fermentation of sugars.* Thus, when yeast is added to a solution of glucose, carbon dioxide and alcohol are formed:



(3) *By reducing metallic oxides with carbon:*

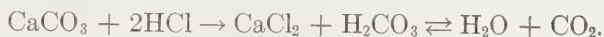


(4) *By heating certain carbonates.* Thus, limestone is heated in kilns to prepare quicklime:



This action is reversible, so in order to secure a high yield of lime the CO_2 must be allowed to escape.

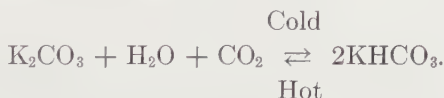
(5) *By treating carbonates with acids:*



This method is the one generally used in the laboratory. Limestone or marble is treated with hydrochloric acid, and the gas is collected over water or by the upward displacement of air. The Kipp apparatus (122) or an ordinary flask with a funnel-tube may be employed. Dilute sulfuric acid is not adapted to the generation of CO_2 from CaCO_3 , for CaSO_4 is formed, which is only slightly soluble. Some CO_2 is produced by the interaction of H_2SO_4 and MgCO_3 (magnesite), MgSO_4 being obtained as a by-product.

Carbon dioxide is obtained as a by-product of the brewing industry.

Carbon dioxide is now produced on a large scale from the flue gases given off during the combustion of fuel, such as coke. The gases are scrubbed, under high pressure, with a solution in which carbon dioxide is soluble, such as a solution of potassium carbonate; potassium bicarbonate is formed:



When the action has gone far enough to the right, the pressure is reduced, and the action is reversed. The escaping carbon dioxide is washed and then stored in cylinders under a pressure of about 1,100 pounds per sq. in.; the potassium carbonate is then ready for a repetition of the process.

433. **Physical Properties.** — Carbon dioxide is a colorless gas with a slightly acid taste and pungent smell. Its sp. gr. (air = 1) is about 1.529, so it is much heavier than air, and, like a liquid, can be poured from one vessel to another. The gas can be readily liquefied, the C.T. being 31.35° and the C.P. 72 atmos. The density of the colorless liquid is 0.9951 at -10° , and its boiling point is -78° . When the stopcock of a cylinder containing liquid carbon dioxide is opened and the opposite end of the vessel slightly elevated, some of the liquid rushes out, a portion of which evaporates and absorbs so much heat that the remaining portion of the liquid is frozen to a crystalline snow-like solid, called "carbonic acid snow." The solid may be collected in quantity by tying a bag of coarse canvas to the nozzle of the tank. Solid

carbon dioxide should not be pressed hard upon the skin, for it will produce a blister similar to a burn. When the solid is mixed with ether and allowed to evaporate, a very low temperature (-100°) is obtained. Thus, mercury may be readily solidified when surrounded by the mixture. Solid carbon dioxide evaporates without melting. Solid carbon dioxide, or "dry ice," is now an article of commerce. At 0° and 760 mm., 1 vol. of water dissolves about 1.8 vols. of carbon dioxide; but at 15° only 1 vol. dissolves. An aqueous solution of carbon dioxide under a pressure of from 3 to 4 atmospheres is known as "soda-water." When such a solution is exposed to the air, it effervesces because of the escape of CO_2 under the reduced pressure.

Animals soon die of suffocation when brought into an atmosphere of carbon dioxide. Air containing abnormally large quantities of the gas should not be breathed for long periods. Large amounts of the gas in the air exert a narcotic effect; it is not particularly poisonous.

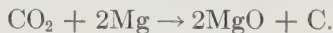
434. Chemical Properties. — Carbon dioxide is a very stable compound. At $2,000^{\circ}$, less than 2 per cent of the molecules are dissociated:



The gas does not burn but, on the other hand, it extinguishes fire. Carbon dioxide may be reduced by passing it over hot carbon:

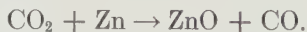


An active metal, such as magnesium or an alkali metal, will burn when ignited in a hollow lump of carbon dioxide:

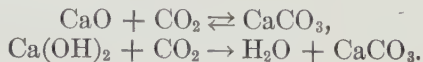


In this case CO_2 is a supporter of combustion.

When carbon dioxide is passed over hot zinc or iron, it is reduced to carbon monoxide:



Carbon dioxide combines readily with oxides or hydroxides of active metals, forming carbonates:



435. **Uses.** — Carbon dioxide is used in the manufacture of soda-water and similar beverages, nearly 60 million pounds having been so used in the United States in 1919. It also is extensively used in the manufacture of washing and baking soda, this industry in our country requiring over 500,000 tons annually.

Solid carbon dioxide, or "dry ice," formed by rapid evaporation of the liquid, is put in steel moulds and pressed into blocks. It is employed as a refrigerant in competition with water ice. Solid carbon dioxide has several advantages: for example, it can be distributed throughout a car-load of fish to keep it frozen in transit for a period of several days; also, small packages of such foods as butter and ice cream may be shipped in paper containers by mail or express.

Carbon dioxide finds additional use for extinguishing fire. In the *portable fire-extinguisher* the gas is generated by bringing together sulfuric acid and a solution of sodium bicarbonate:



In baking bread, CO_2 is formed, and escapes from the dough, causing the bread to rise. Much CO_2 is consumed in the production of white lead (608). It plays a great rôle in nature.

436. **The Carbon — Carbon Dioxide — Oxygen Cycle.** — Carbon and carbon dioxide are very closely related to life. Carbon and oxygen are great carriers of energy, and when they unite to form carbon dioxide a large amount of heat is liberated. The oxidation of carbon with the production of heat occurs not only during combustion and decay, but in the bodies of animals during respiration. The carbon dioxide of the air is reduced in the green leaves of plants, the carbon being appropriated, along with water, to form cellulose and starch, the oxygen being returned to the air. The radiant energy of the sun is the source of the required energy, and the green coloring matter of leaves (chlorophyll) and the protoplasm take part in the transformation. The radiant energy of the sun is therefore transformed into the storable form of chemical energy. It is clear now why it is so essential to have as large a portion as possible of the earth's crust covered with green plants.

The chemical equation for the transformation of CO_2 into cellulose and starch may be written thus:



When a mol of cellulose or starch is oxidized, the same quantity of heat is liberated. As a matter of fact, the change is more complicated than that represented by the equation; but it gives an idea as to the essential reaction occurring.

Carbon dioxide is, therefore, an essential food for plants, and the oxygen returned to the air is available for repeating the cycle.

437. Carbonic Acid and Carbonates. — When carbon dioxide is dissolved in water, some of the compound unites with water to form the weak, unstable *carbonic acid*:



Carbon dioxide is frequently called carbonic anhydride, or carbonic acid gas. Carbonic acid has never been obtained in the free state, being known only in solution. It is dibasic and is one of the feeblest of acids.

With each metal it forms two salts — an acid salt and a normal or neutral salt. Thus, we have acid sodium carbonate, NaHCO_3 , and sodium carbonate (washing soda), $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$; also calcium bicarbonate, $\text{Ca}(\text{HCO}_3)_2$, and calcium carbonate, CaCO_3 . (State the conditions under which these salts may be formed.)

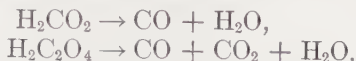
The behavior of limestone in the presence of natural waters containing carbon dioxide makes it easy to understand the formation of caves, such as the Mammoth Cave in Kentucky. On account of the slow action of carbonic acid, soluble calcium bicarbonate is formed (see Hard Waters, 148), and in the course of time much of the rock is eaten away, leaving a cave. When the solution loses carbon dioxide at the roof of the cave, calcium carbonate is left behind as a sort of stony icicle called *stalactite*; but when drops of water fall to the bottom of the cave, evaporation occurs with further loss of carbon dioxide, and deposits of calcium carbonate are formed which are known as *stalagmites*. The stalactites and stalagmites may unite, forming pillars or columns. A limestone cave therefore has a tendency to refill itself.

In Kents Cavern, near Torquay, England, certain stalagmites are being built up at the rate of one inch in 1,000 years. One stalagmite in this cavern is 4.5 feet in height, and the period of its formation is probably over 50,000 years.

CARBON MONOXIDE, CO

438. Preparation. — Carbon monoxide can be prepared conveniently for laboratory use *by treating either formic acid (H_2CO_2) or oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) with concentrated sulfuric acid.* The acids

are heated in a flask, and the sulfuric acid abstracts the elements of water. In the case of oxalic acid carbon dioxide is also formed:



If oxalic acid is used, the carbon dioxide may be removed by passing the gas through a solution of an alkali.

Carbon monoxide also may be prepared by *passing carbon dioxide over red-hot carbon*:



Any remaining carbon dioxide may be removed by washing the gas with a solution of an alkali. Carbon monoxide is collected over water. This method for preparing carbon monoxide explains the formation of the gas in an ordinary grate fire, where reduction occurs in the interior of the grate as the dioxide passes over heated carbon. The monoxide, on coming in contact with air at the top of the grate, burns with a blue flame to form the dioxide. Carbon monoxide is formed in ranges, stoves, and furnaces during incomplete combustion and may escape into a room in case of insufficient draft (Fig. 142). The gas is also formed in the combustion engine, especially when the "choker" is pulled out, due to the fact that there is an excess of gasoline and combustion or oxidation is not complete. Since carbon monoxide is highly poisonous, a combustion engine should not be operated in a closed garage.

Carbon monoxide, mixed with hydrogen, is obtained by blowing steam over white-hot carbon (coke or anthracite):



The mixture of hydrogen and carbon monoxide is called *water gas*; it is not pure, for it contains carbon dioxide and nitrogen. CO may be separated from H₂ by liquefying the former.

Producer gas (approximately 39 per cent of CO and 60 per cent of N₂) is made when air is passed over heated coke. Water gas and producer gas are excellent fuels.

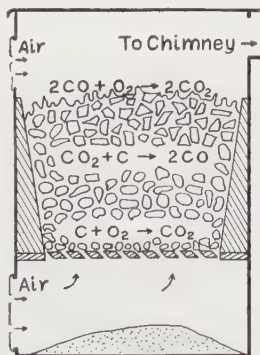


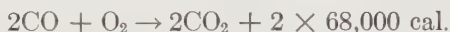
FIG. 142.

439. **Physical Properties.** — Carbon monoxide is a colorless gas and practically odorless and tasteless. The gas is only very slightly soluble in water and is difficult to liquefy. It closely resembles nitrogen in physical properties, as shown below.

COMPARISON OF THE PHYSICAL PROPERTIES OF NITROGEN AND OF CARBON MONOXIDE

	Mol. Wt.	Sp. Gr. (air)	C.P.	C.T.	B.P.	M.P.
N ₂	28	0.967	33.5 atmos.	-147°	-195.5°	-210.5°
CO.....	28	0.967	35.5 atmos.	-139.5°	-190.0°	-211.0°

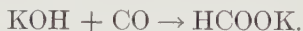
440. **Chemical Properties.** — Carbon monoxide is an unsaturated compound, *i.e.*, it has a tendency to combine with such substances as oxygen and chlorine in order that carbon may have its maximum valence of 4. The gas burns with a bluish flame, producing much heat:



Carbon monoxide is a good reducing agent and thus plays an important rôle in the blast furnace:



Carbon monoxide is readily absorbed by an ammoniacal or hydrochloric acid solution of cuprous chloride, a fact of importance in gas analysis. It also unites directly with hot potassium hydroxide to form *potassium formate*:

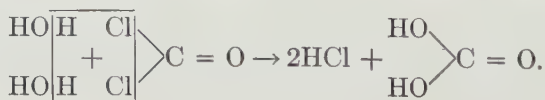


When a mixture of carbon monoxide and chlorine is exposed to sunlight, the gases unite to form **phosgene** (Greek, *generated by light*), or **carbonyl chloride** (275):



It is manufactured by passing CO and Cl₂ over porous charcoal (catalyst).

Phosgene is a colorless liquid with a low boiling point (8°), and its vapor is very poisonous; it was used very extensively during the Great War. When phosgene comes in contact with water, it hydrolyzes:



When it is inspired, therefore, hydrochloric acid is formed in the lungs. Phosgene is used in the production of coloring matter and in synthetic chemistry.

Carbon monoxide unites directly with nickel and iron to form nickel and iron *carbonyls* $\text{Ni}(\text{CO})_4$ and $\text{Fe}(\text{CO})_4$.

The composition of carbon monoxide by volume may be established by exploding a mixture of the gas with oxygen, 2 vols. of the gas uniting with 1 vol. of oxygen to give 2 vols. of carbon dioxide. This fact, coupled with the weight of 1 mol of the gas (28 g.), shows that its formula is CO.

441. **Physiological Action.** — Carbon monoxide is a very poisonous gas; it unites with the hemoglobin of the blood corpuscles to form *carbonyl-hemoglobin*, a stable compound, which shuts off the supply of oxygen. One vol. of CO to about 800 vols. of air will produce death in about 30 minutes, while 1 vol. in 100,000 vols. of air produces symptoms of poisoning. Birds and mice are more sensitive to its action than is man.

Hopcalite, a mixture of metallic oxides, is used in gas masks to oxidize CO, serving as a catalyst.

CARBON DISULFIDE, CS_2

442. **Preparation.** — *Carbon disulfide* is prepared by the direct union of highly heated charcoal and the vapor of sulfur.



Some carbon disulfide is manufactured in the electric furnace (Taylor process), the electrical energy being the source of heat. The vapor of carbon disulfide is easily condensed to the liquid state.

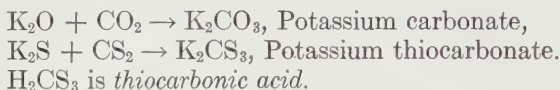
443. **Properties and Uses.** — Carbon disulfide is a liquid, which boils at 46° . When pure, it is colorless and has a pleasant odor; it is not very stable, however, so it ordinarily has a disagreeable odor. Carbon disulfide has a high index of refraction, a density of 1.292, and is only slightly soluble in water. Its vapor is very inflammable, when mixed with air, and the kindling temperature is low (probably under 200°):



Its vapor is also poisonous. Great care must be exercised, therefore, in handling the substance.

CS_2 is a good solvent for fats, resins, rubber, sulfur, and iodine. It is employed extensively as a solvent, for the manufacture of carbon tetrachloride and rayon (751), and for the extermination of burrowing animals, such as the prairie dog and the rat, and as an insecticide.

It is interesting to note that CS_2 is analogous to CO_2 :



444. Carbon Tetrachloride, CCl_4 . — This compound is manufactured by passing dry chlorine gas into carbon disulfide containing a trace of iodine (catalyst):

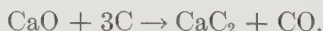


The boiling point of CCl_4 is 77° and that of S_2Cl_2 is 136° ; therefore the liquids may be separated by fractional distillation. Sulfur chloride is a good solvent for sulfur, and is used extensively in vulcanizing rubber.

Carbon tetrachloride is a colorless liquid with a pleasant odor. It is non-inflammable, a good solvent for fats, oils, etc., and is largely used for this purpose instead of inflammable benzene, gasoline, or carbon disulfide. A great deal of carbon tetrachloride is used in fire extinguishers, being sold under the name of **pyrene**. Carbon tetrachloride, mixed with benzene, is used in dry-cleaning and for removing stains.

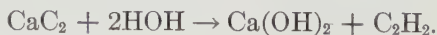
CARBIDES

445. Calcium Carbide, CaC_2 . — Calcium carbide is prepared by heating a mixture of pulverized lime and coke in an electric furnace (Fig. 171):



The carbide forms as a liquid and is drawn off from time to time.

Commercial calcium carbide is a hard, brittle, dark-gray, crystalline mass. When pure, it is quite colorless and transparent. It reacts with cold water with great readiness, forming *acetylene*:

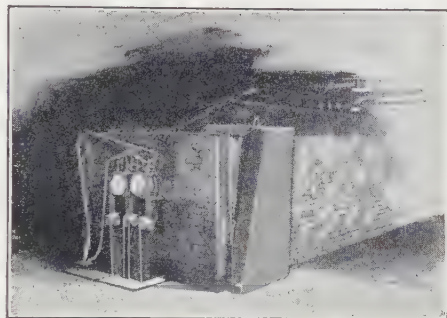


It also combines, at high temperatures, with nitrogen to form *calcium cyanamide* (358), which is used as a fertilizer and in the manufacture of ammonia and nitric acid (376).

446. Silicon Carbide, or Carborundum, SiC. — This compound is manufactured at Niagara Falls by the Acheson process. Sand, coke, and common salt, to which a little sawdust may be added, are heated in an electric furnace for about 36 hours (Fig. 143). The charge is packed around a horizontal core of granulated coke. The equation for the reaction is as follows:



The crystals often have a beautiful, iridescent luster, but they may vary from black to green, to practically colorless. It is extremely hard, being harder than corundum.



Courtesy, Carborundum Co.

FIG. 143. A Carborundum Furnace.

Silicon carbide is decomposed at $2,200^{\circ}$, is stable in the air, not attacked by acids, but is decomposed by fusion with caustic alkalis.

Carborundum, mixed with clay or other materials as a binder, is used very extensively in the manufacture of abrasives, such as grinding wheels, whetstones, etc.

There are many other valuable products of the electric furnace, in which electricity is transformed into heat.

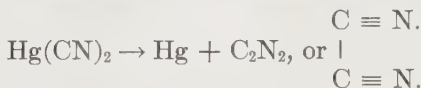
The Cowles Electric Smelting and Aluminium Company, of Cleveland, first employed (1885) the electric furnace on a large scale. Moissan, of Paris, employed the furnace, in 1893, in the preparation of artificial diamonds from carbon.

The first carborundum furnace produced only a quarter of a pound per day, which sold at 80 dollars a pound. A modern furnace can produce 16,000 pounds in 36 hours, which sells for about 15 cents a pound. The annual production is about 30,000 tons. This is an excellent illustration of the possibilities of utilizing the heat of the electric furnace. Electrochemistry is one of the most important branches of chemistry.

CYANOGEN, CYANIDES, AND CYANATES

447. Cyanogen, C_2N_2 . — The *cyanide radical* (CN) has a valence of 1, and in the formation of compounds may be treated as an atom of chlorine (Cl).

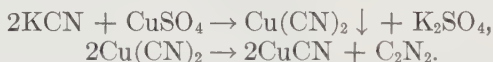
Cyanogen (Greek, *blue + to produce*) gas may be prepared by heating mercuric cyanide in a hard glass test-tube (97):



Cyanogen is possibly formed in small amount when electricity is discharged between carbon poles in an atmosphere of nitrogen:

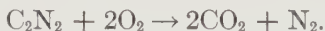


The gas may be readily prepared by allowing a solution of copper sulfate slowly to flow into a solution of potassium cyanide:



The cupric cyanide, at first precipitated, is unstable and decomposes, forming cuprous cyanide and cyanogen.

Cyanogen is a colorless gas with the odor of peach kernels. The gas is extremely poisonous, and burns with a purple flame:



448. Cyanides. — These compounds are somewhat analogous to chlorides:

	<i>Chlorides</i>		<i>Cyanides</i>
HCl.....	Hydrogen chloride	HCN.....	Hydrogen cyanide
KCl.....	Potassium chloride	KCN.....	Potassium cyanide
HgCl ₂	Mercuric chloride	Hg(CN) ₂ ..	Mercuric cyanide

Hydrocyanic (prussic) acid, HCN, is found in combination in leaves of the laurel and cherry and in the kernels of the cherry, peach, etc. It may be prepared by treating a cyanide with sulfuric acid:



The vapor may be collected in water, or condensed to a colorless liquid, boiling at 26°. It has the odor of bitter almonds and is extremely poisonous! A good antidote is freshly precipitated ferrous hydroxide, ammonia being administered as a stimulant. When hydrocyanic acid vapor is inspired, air containing chlorine may be employed as an antidote. The vapor burns, giving a

peach-blossom colored flame:



Hydrocyanic acid is an extremely weak acid (see Hydrolysis, 257).

Two *constitutional formulae* have been suggested for the acid:

Hydrogen cyanide, $\text{H} - \text{C} \equiv \text{N}$; or

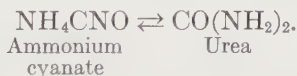
Hydrogen isocyanide, $\text{H} - \text{N} \equiv \text{C}$.

Organic derivatives corresponding to both formulae have been prepared, being known as *isomers* (719 and 725). The cyanides are reducing agents.

449. **Cyanates.** — A cyanate may be formed by reducing a metallic oxide by means of a cyanide. Thus, when a mixture of lead oxide and potassium cyanide is heated, potassium cyanate (KCNO) is formed:



The German chemist Wöhler (1828) obtained urea by warming a solution of ammonium cyanate:



This reaction is of great historical interest, for it was the first time an organic compound was prepared in the laboratory. Ammonium cyanate and urea are isomers, but their properties are different owing to the different arrangement of the atoms constituting the molecule of each.

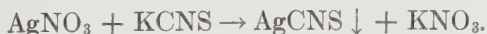
Cyanic acid, HCNO, is a colorless liquid, stable below 0°.

Potassium thiocyanate, KCNS, may be obtained by boiling a solution of potassium cyanide with sulfur:



Solutions of alkali thiocyanates are used as a test for ferric iron (211). *Thiocyanic acid*, HCNS, is analogous to cyanic acid. At 0° it forms a white crystalline solid, melting at about 5°.

When a solution of a silver salt is treated with a solution of potassium thiocyanate, a white cheese-like precipitate is obtained, which is insoluble in mineral acids (see AgCl):



EXERCISES

1. Show the relation of carbon to silicon. Name the other elements occupying the same group.
2. Describe the allotropic forms of carbon. How are graphite and charcoal (animal and vegetable) manufactured? How can it be proved that a pure diamond is carbon? How did Moissan prepare diamonds?
3. What conclusions may be drawn from the fact that diamonds and silicon carbide have been found in the Cañon Diablo Meteorite? What conclusion may be drawn from the fact that more diamonds are found in fragments and splinters than in perfect crystals?
4. Cite evidence to show that diamonds may have crystallized out from a lava or magma consisting mainly of magnesium silicates.
5. Why is coal thought to be of vegetable origin? Describe three kinds of coal and point out the difference in their carbon content.
6. What is meant by destructive distillation? How may the following substances be prepared: coke, lampblack, gas-carbon, carbon-black?
7. Give the properties of charcoal. Explain as fully as you can, also illustrate, what is meant by adsorption. What are the chemical properties of carbon? How is carbon "activated"?
8. Outline the history leading up to the discovery of carbon dioxide, including the classical investigations of Joseph Black.
9. How is carbon dioxide produced industrially? What is "dry ice," and what principle is employed in its production?
10. Show that carbon dioxide will support the combustion of certain substances. Why does it extinguish fire?
11. Outline the great rôle played by carbon dioxide in nature.
12. How would you prove that carbonic acid is a weak, dibasic acid? Explain what action, if any, aqueous solutions of NaHCO_3 and of Na_2CO_3 have upon litmus.
13. Outline several ways in which carbon monoxide may be formed. State its physical properties. Write chemical equations to show its chemical properties.
14. Explain the physiological action of carbon monoxide. How may it be removed from air?
15. Outline the preparation of carbon disulfide. State its properties, and show that it is analogous to carbon dioxide. For what is it used?
16. (a) Outline methods for the preparation of two very important carbides and state their properties and uses.
(b) Give the preparation, properties, and uses of carbon tetrachloride.
17. How may cyanogen and hydrocyanic acid be prepared? State their physical and chemical properties. Show the relation of cyanides to halides.
18. For what are KCN and NaCN used? Why are their aqueous solutions strongly alkaline? Show that they are reducing agents.
19. What are cyanates? What is the relation of ammonium cyanate to urea? Point out the significance of the discovery made by Wöhler in 1828.
20. When a solution of potassium ferrocyanide is treated with an excess of hot sulfuric acid, the products are carbon monoxide and potassium, ammonium and ferrous sulfates. Write the equation for the reaction. What weight and what volumes of carbon monoxide, measured over water at 21°C . and 772 mm., could be obtained from 1.5 mols of potassium ferrocyanide, $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$?

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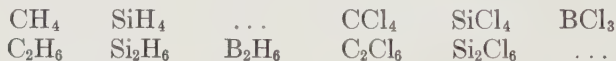
CHAPTER XXV

SILICON AND BORON. REVIEW OF THE NON-METALS

450. Relationships and General Characteristics. — We have seen (418) that silicon belongs to Group IV, being closely related to carbon. Boron belongs to Group III, and is a member of the Aluminium Family (580). Both aluminium and boron are trivalent, but boron is a pronounced non-metallic element, while aluminium is amphoteric in character. Thus, B_2O_3 and $B(OH)_3$ are acidic, the latter being boric acid and the former its anhydride. Al_2O_3 and $Al(OH)_3$ are analogous to B_2O_3 and $B(OH)_3$, but $Al(OH)_3$ is an amphoteric hydroxide, *i.e.*, it may function either as a base or an acid.

In its chemical relations boron resembles carbon and silicon more closely than it resembles aluminium: *e.g.*, all of them exhibit allotropic forms, and combine directly with oxygen at a high temperature to form anhydrides of feeble acids — B_2O_3 , CO_2 , and SiO_2 .

All three elements form hydrides, as well as binary halogen compounds:



Boron combines with carbon and with silicon at the temperature of the electric furnace to form the carbide B_6C and the silicides B_6Si and B_3Si , which are very refractory and crystalline, being somewhat similar to the diamond and to crystalline boron and silicon. Carbon and silicon are much more abundant than boron and are more widely distributed in nature.

SILICON. Si = 28.06

451. Occurrence. — Next to oxygen, silicon is the most abundant element, constituting a little more than one-fourth of the mass of the earth's crust. The element does not occur in the free state, but in combination with oxygen and other elements it is very widely distributed. Since silicon compounds play such

an important part in the formation of the minerals and rocks which constitute so much of the earth's crust, it may be regarded as the central element of the Inorganic Kingdom, just as carbon is the central element of the Organic Kingdom.

Silica and silicates are the most abundant minerals constituting the earth's crust.

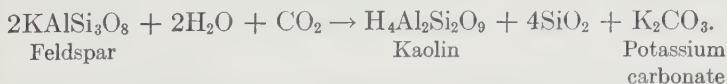
For convenience of study F. W. Clarke divides the crust of the earth into three shells or layers:

(1) *The innermost shell*, which consists of plutonic or igneous rocks of crystalline structure, and has unknown thickness. The compositions of these rocks are the nearest approach to the original materials.

(2) *Sedimentary and fragmentary rocks*. This shell overlies the innermost shell, being rather thin.

(3) *Soils, clays, gravels, etc.* This also is a thin layer.

The material of the second and third layers is derived chiefly from the first, due to the weathering and disintegration of the rock. It is believed that the central mass of the earth constitutes more than half of its entire mass. Overlying this central mass there is a lighter mass of silicates, the composition of which appears to correspond to that of igneous rocks. The heavier silicates of iron, aluminium, and magnesium probably form the lower layers, while the lighter silicates of calcium, potassium, and sodium are above. Quartz or silica (SiO_2) is still higher up. It is probable that all the silicates, except the uppermost, are in the molten state, and they correspond to the magmas erupted by active volcanoes. Magma solidifies to form igneous rocks. Rocks are gradually broken down by exposure to natural agencies, the change being partly mechanical and partly chemical. Water, carbon dioxide, and animal and vegetable life all play an important part in this disintegration which has been going on for countless ages. The most abundant minerals occurring in igneous rocks are the **feldspars**. Potash feldspar (KAlSi_3O_8) and soda feldspar ($\text{NaAlSi}_3\text{O}_8$) are very abundant and important. When feldspars weather, kaolin or clay, silica, and potassium carbonate are formed:

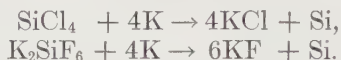


This reaction is of prime importance in the formation of soil.

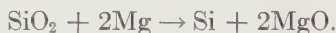
Rocks are the fundamental units of geology, and are either simple minerals or aggregations of minerals. Rocks are usually

mixtures and are therefore variable in composition. Thus, granite is a mixture of quartz, feldspar, and mica. The minerals which most commonly take part in rock formation are the very stable ones of the abundant elements: *e.g.*, quartz or silica (SiO_2). The chemistry of silicon is fundamental in the study of mineralogy and geology.

452. **Preparation.** — Silicon was first prepared by the Swedish chemist, Berzelius, in 1823. Although it is a very abundant element, it is rather difficult to prepare. The element may be obtained by the interaction of silicon tetrachloride or potassium fluosilicate (K_2SiF_6) and potassium, sodium, or aluminium, at a high temperature. The action is carried out so as to prevent oxidation. The chemical changes may be represented thus:

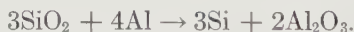


When the potassium salts are dissolved in water, silicon remains, usually as a brown powder. Silicon is conveniently prepared in the laboratory by heating a mixture of finely divided silica and magnesium:



A small amount of magnesium silicide, Mg_2Si , is also formed. Magnesium oxide may be readily separated from silicon by the addition of hydrochloric acid. The silicon is obtained in the form of a brown powder.

When aluminium is substituted for magnesium, silicon may be obtained in the form of larger crystals:



The free silicon crystallizes in the excess of molten aluminium as it solidifies.

Silicon is prepared industrially by heating silica and coke to a high temperature in the electric furnace:



With excess of carbon, carborundum (SiC) is formed (446).

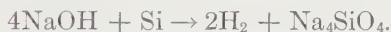
When a mixture of oxide of iron, silica, and carbon is heated in the electric furnace, both oxides suffer reduction, forming **ferrosilicon**, an alloy used in the manufacture of steel. An alloy

called "duriron" contains 14 per cent of silicon; it is very resistant to corrosion by acids.

453. **Properties and Uses.** — The so-called "amorphous" silicon is a brown powder, which melts at $1,420^{\circ}$. X-ray analysis shows it to be crystalline; it differs from massive silicon only in subdivision.

Silicon is an exceedingly hard substance, easily scratching glass, and possessing a density of 2.35; it is gray-black, lustrous, and brittle (see the Diamond).

Silicon is quite reactive, particularly at high temperatures. In its chemical properties it closely resembles carbon. With the halogens it forms compounds (SiF_4 , SiCl_4). On heating in air, silicon burns to form SiO_2 . It is dissolved by hot caustic alkalies forming hydrogen and a silicate:



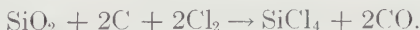
Hydrogen for filling balloons may be prepared by this method.

Silicon at high temperatures combines directly with most of the elements, forming *silicides*: e.g., Mg_2Si , magnesium silicide; CSi , carbon silicide or silicon carbide.

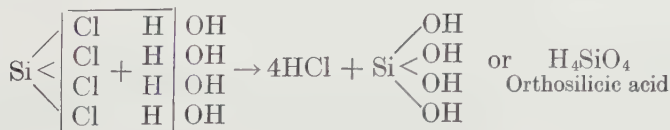
Silicon is used as a deoxidizer in making castings of steel, copper, or bronze; it also is a constituent of important alloys, such as duriron. It is a constituent (11–13 per cent) of a new class of aluminium alloys. Commercially pure cast silicon has been produced for chemical containers.

COMPOUNDS OF SILICON

454. **Silicon Tetrachloride, SiCl_4 .** — Silicon chloride is prepared by passing chlorine gas through a heated mixture of silica and carbon:



It is a colorless liquid, boiling at 59° . When brought in contact with moist air, it hydrolyzes, forming hydrochloric acid and orthosilicic acid (298):



During the Great War silicon tetrachloride was used on a large scale in the production of smoke clouds. It is particularly effective when used in connection with ammonia, for white clouds of ammonium chloride (NH_4Cl) are formed.

455. **Silicon Tetrafluoride; Fluosilicic Acid.** — Silicon tetrafluoride, which is formed when hydrofluoric acid acts upon silica (302), is a colorless gas, readily decomposed by water, forming silicic acid and *fluosilicic acid* (H_2SiF_6):



Silicic acid may be removed by filtration, a solution of fluosilicic acid being left. This acid is known only in solution, for when its solution is concentrated by evaporation, silicon tetrafluoride is given off:



Most of the salts of fluosilicic acid are soluble in water, conspicuous exceptions being K_2SiF_6 and BaSiF_6 , which are sparingly soluble in water and insoluble in alcohol. The acid is therefore used in analysis for separating certain of the metals.

456. **Silicon Dioxide or Silica, SiO_2 .** — Silicon dioxide occurs in great abundance and very widely distributed. The chief forms of silica, which are more or less pure, are as follows:

(I) Crystalline	(II) Massive	(III) Fragmentary
Rock Crystal	Quartzite	Sea Sand
Amethyst	Rose Quartz	Gravel
Smoky Quartz	Agate	Pebbles
Tridymite	Jasper	Sandstone
	Carnelian	Conglomerate
	Flint	
	Chalcedony	
	Opal	

Silica is found abundantly as *diatomaceous (infusorial) earth*, or *kieselguhr*. This is an opal-like silica secreted by organisms, as the shells of diatoms. Deposits of diatomaceous earth are found in Maryland, Virginia, Missouri, Alabama, and California. It is used as an absorbent for nitroglycerine, as a wood filler, as a polishing powder, etc.

Silica occurs in the hard parts of straw, bamboo, etc., and as petrified wood.

The colored varieties of silica owe their color to small quantities of impurities. Thus, the color of amethyst is due to manganese

and iron, and that of smoky quartz to organic matter. Opal and flint are slightly hydrated forms of silica.

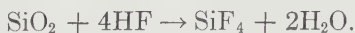
Quartz crystallizes in six-sided prisms capped with pyramids; its sp. gr. is 2.65 and the hardness is 7 (Fig. 144). Clear crystals of quartz are used in the manufacture of optical instruments and spectacles. The melting point of quartz is $1,600^{\circ}$; therefore it fuses in the oxyacetylene flame and in the electric furnace. Chemical apparatus is now manufactured by fusing quartz. When it is fused in the oxyhydrogen or oxyacetylene flame, the product is



FIG. 144. Quartz Crystals. Magnet Cove, Arkansas. Jesup Gift, American Museum of Natural History.

transparent; but when fused in the electric furnace, gas bubbles appear, giving articles made from it a milky appearance. Quartz has the lowest coefficient of expansion of any known substance (0.000000449 between 0° and $1,000^{\circ}$); therefore quartz vessels may be heated to redness and suddenly chilled without cracking. This may be strikingly shown by heating a quartz dish or tube to redness and then plunging it into ice water. "Silica ware" is employed in considerable quantities.

Silica is quite resistant to the action of most chemical reagents. It is readily attacked by hydrofluoric acid, forming silicon tetrafluoride:



Silica may be volatilized completely by heating it in a platinum crucible with this acid. Silica interacts with hot alkalis or alkali

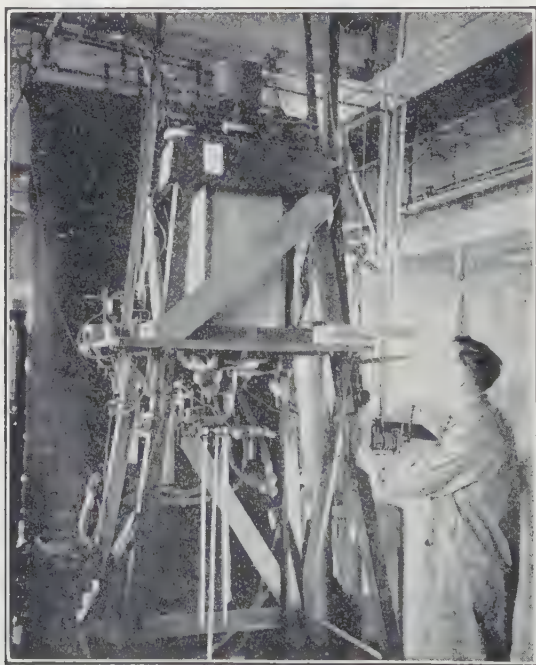
carbonates to form soluble silicates:



Quartz, sand, clay, feldspar, etc., are transformed into soluble substances by fusion, best in platinum crucibles, with alkali carbonates (Na_2CO_3 , K_2CO_3). This is an important and common operation in analysis.

The silicates of the alkali metals are soluble in water, and are called "soluble glass" or "water glass."

457. **Silica Glass or Fused Quartz.** — Clear fused quartz is now produced industrially by means of an electric vacuum furnace



Courtesy, General Electric Co.

FIG. 145. Electric Vacuum Furnace for the Production of Transparent Quartz.

(Fig. 145). Very pure quartz is melted in the furnace, the quartz flowing away in the form of rods or tubing. Indeed, comparatively large masses of perfectly clear quartz may be produced. Accord-

ing to Elihu Thomson, quartz produced by this fusion process is probably the most transparent substance in existence. It is remarkable for its transparency to rays of the visible spectrum, to low heat or ultra-red rays, as well as to the ultra-violet invisible rays. Rods of quartz may be employed to convey ultra-violet rays to the cavities of the body in order to treat diseased areas, such as the ear, the nasal cavity, and the throat. A rod of fused quartz as much as 26 feet in length will convey, by internal reflection, the light of a match from one end to the other. Even bent rods convey heat and light. Fused quartz is the ideal glass. It is used in the construction of prisms, lenses, windows, etc.

458. Oxyacids of Silicon. — Salts (*silicates*) of a number of acids of silicon are known, but none of the acids has been obtained in the pure state. *Silicon dioxide is the anhydride of all the oxyacids of silicon.* We have seen that silicon tetrachloride (454) hydrolyzes to form *orthosilicic acid* (H_4SiO_4). This acid may be regarded as containing potentially two molecules of water and one of the anhydride:



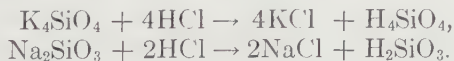
Orthosilicic acid is unstable and when an attempt is made to separate it from water, it readily loses one molecule of water to form *metasilicic acid* (H_2SiO_3):



This acid is the analogue of carbonic acid, H_2CO_3 .

The silicic acids are very feeble. Salts of orthosilicic acid are called orthosilicates (*e.g.*, K_4SiO_4), while those of metasilicic acid are metasilicates (*e.g.*, Na_2SiO_3).

The silicates of the alkali metals are readily decomposed by acids:



When a concentrated aqueous solution of a silicate of an alkali metal, *e.g.*, sodium silicate, is treated with an acid, such as hydrochloric, silicic acid is set free as a gelatinous mass (*hydrogel*, or *gel*); but when the solution of the silicate is poured into concentrated hydrochloric acid, no precipitate appears. The silicic acid is in colloidal suspension. So long as the colloid appears to be in solution, it is called a *hydrosol*, or a *sol*. Thomas Graham (1861) divided chemical substances into two classes:

(1) **Crystalloids.** This class includes substances which may be obtained in crystalline form: *e.g.*, salt, sugar, potassium nitrate. Solutions of such substances not only pass through filters, but diffuse through parchment paper or an animal membrane.

(2) **Colloids.** These substances, according to Graham, do not crystallize: *e.g.*, silicic acid, gums, starch, gelatin, glue, etc. The word *colloid* is derived from the Greek word *kolla* (glue) + *-oid*. A colloidal solution passes through ordinary filters, leaving no solid. If, however, a fine parchment paper or an animal



FIG. 146.

membrane be substituted for the filter paper, the colloid is retained and the crystalloid passes through. Graham invented a **dialyzer** which he employed to separate crystalloids from colloids (Fig. 146).

The parchment paper or membrane (C) is stretched on a tambourine-like frame (A), and the colloidal solution is poured into the dialyzer, which is partially immersed in a larger vessel (B) containing pure water. When, therefore, a solution containing sodium chloride and silicic acid is placed in a dialyzer, the salt passes through the membrane into the water, while silicic acid is retained.

The subject of colloids will be discussed more fully in the next chapter.

When a solution of a stable salt and silicic acid is evaporated to dryness and the residue ignited, the acid undergoes dehydration, and a mixture of the salt and silica is obtained:



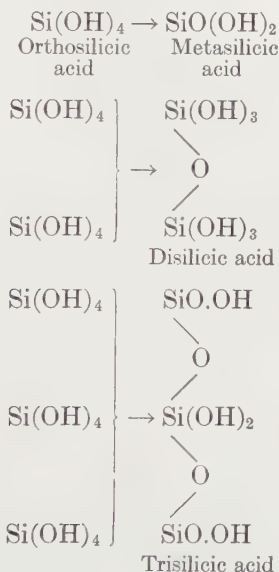
Thus, when a solution of sodium silicate is acidified with hydrochloric acid and then evaporated to dryness and gently ignited, a residue consisting of NaCl and SiO₂ is obtained. On addition of water the salt goes into solution, leaving SiO₂ as a residue.

459. **Polysilicic Acids.**—Many complex silicates occur as minerals and rocks, being called salts of polysilicic acids. These acids may be derived from two or more molecules of orthosilicic acid by the loss of water, and are called *condensed acids*. The following may serve as illustrations:



When heated they all gradually lose water, forming in the end the anhydride SiO_2 .

The relationships of some of the acids of silicon may be shown as follows:



460. **The Naturally-Occurring Silicates.** — The following list includes some of the most important silicates which occur in the mineral kingdom:

- | | |
|---|---|
| (I) <i>Metasilicates</i>
(Salts of H_2SiO_3) | { CaSiO_3 , Wollastonite
$\text{Mg}_3\text{H}_2(\text{SiO}_3)_4$, Talc |
| (II) <i>Orthosilicates</i>
(Salts of H_4SiO_4) | { Mg_2SiO_4 , Olivine
$\text{Al}_2\text{H}_2(\text{SiO}_4)_2 \cdot \text{H}_2\text{O}$, Kaolin
$\text{KAl}_3\text{H}_2(\text{SiO}_4)_3$, Mica |
| (III) <i>Disilicates</i> : e.g., $\text{Mg}_3\text{Si}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$, Serpentine
(Salts of $\text{H}_6\text{Si}_2\text{O}_7$) | |
| (IV) <i>Trisilicates</i>
(Salts of $\text{H}_4\text{Si}_3\text{O}_8$) | { KAlSi_3O_8 , Potash feldspar
(orthoclase)
$\text{NaAlSi}_3\text{O}_8$, Soda feldspar (albite). |

As previously stated, many rocks are complex silicates or mixtures of silicates. For instance, **pyroxene** and **amphibole** (includ-

ing asbestos) are silicates of calcium and magnesium; **trap rock** contains pyroxene and feldspar; **garnet** is $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_3$; **gneiss**, like granite, is a mixture of quartz, feldspar, and mica; and some feldspars contain both potassium and sodium $(\text{K}, \text{Na})\text{AlSi}_3\text{O}_8$.

The silicates frequently contain alumina, as well as silica, combined with a powerful base. Since alumina is amphoteric in nature, it may function as an acid anhydride in forming certain silicates, just as does silica. The composition of a silicate such as feldspar may be represented thus:



Many naturally-occurring silicates, such as talc, mica, kaolin, feldspar, and asbestos, are of great commercial importance.

461. The Manufacture of Silicates. — The *glasses*, which are silicates, or mixtures of silicates, or of silicates and silica, are obtained by fusing silica with such substances as sodium carbonate (or potassium carbonate), or with these salts and limestone.

The simplest glass is *water glass*, or *soluble glass*. Water glass is sodium silicate (ortho- or meta- or a mixture of these silicates). It may be prepared (1) by fusing powdered quartz or infusorial earth with NaOH or Na_2CO_3 (456); or (2) by boiling SiO_2 in a digester with a solution of NaOH under pressure.

Water glass is soluble in water, and the solution has an alkaline reaction (why?). For commercial use, the salt Na_2SiO_3 is rendered less alkaline by increasing the proportion of SiO_2 . The composition of ordinary water glass may vary from $\text{Na}_2\text{SiO}_3 \cdot \text{SiO}_2$ to $\text{Na}_2\text{SiO}_3 \cdot 3\text{SiO}_2$. It is used as a filler in cheap soaps, for fire-proofing and water-proofing textiles and timbers, and for preserving eggs. For the last purpose a solution consisting of 1 vol. of ordinary water glass to 9 vols. of pure water is of appropriate concentration. The solution is a poor solvent for gases and possesses a low vapor pressure. Fresh eggs may be preserved in such solutions for long periods.

462. Glass. — Ordinary glasses contain two or more silicates and an excess of silica. They are hard, brittle, and transparent, and are virtually insoluble in water and in acids, with the exception of hydrofluoric acid. They may be divided into three general classes:

(1) **Window or Bottle Glass.** This variety of glass is produced by fusing a mixture of "soda ash" (Na_2CO_3), quartz sand, and limestone:



In the manufacture of cheap glass, "salt cake" (Na_2SO_4) may be substituted for Na_2CO_3 . Sodium-calcium glass is soft, for it may be readily softened by heat.

(2) **Hard or Bohemian Glass.** This is a potash glass, and may be produced by substituting potassium carbonate for sodium carbonate. This variety of glass is difficult to fuse, being used extensively in the manufacture of chemical apparatus. In the production of Jena and "non-sol" glass, boric anhydride (B_2O_3) and zinc oxide are used in addition to silica. *Pyrex glass* is very resistant to heat and shock. It is a sodium-aluminium borosilicate containing excess of silica.

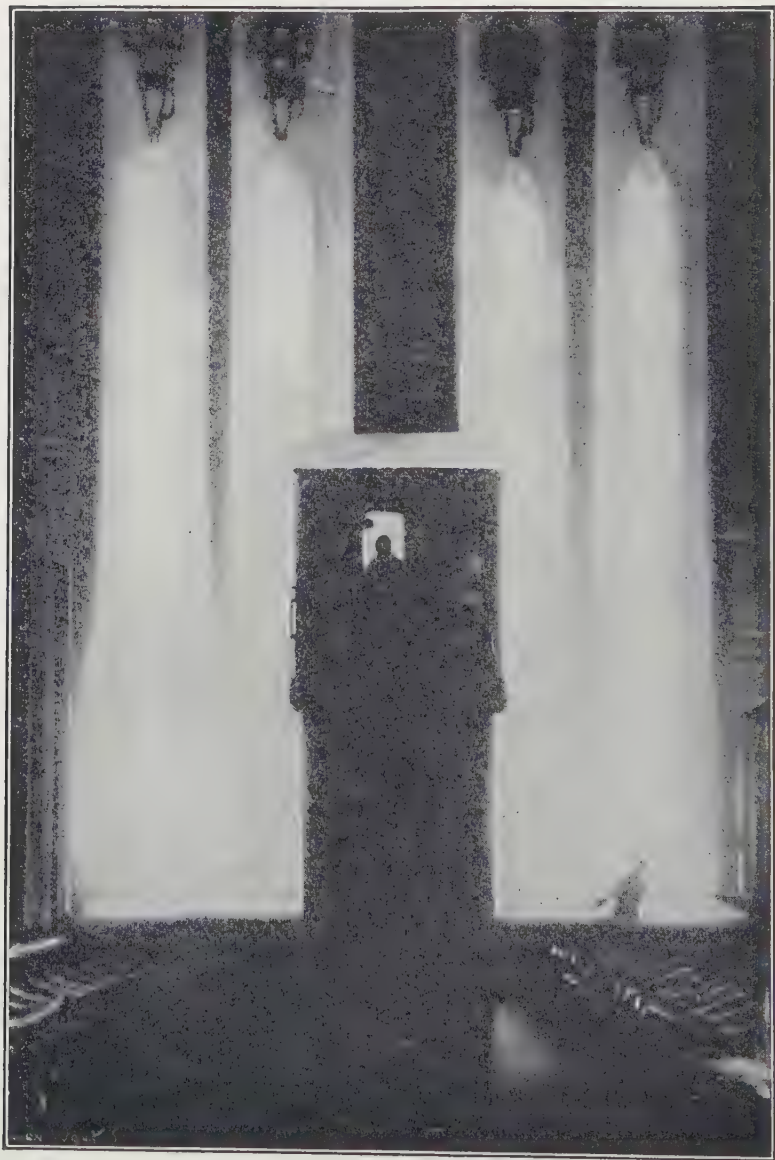
(3) **Flint Glass.** In the production of this variety of glass, lead oxide is substituted for calcium oxide, or lime, which is supplied by limestone. The potash-lead glass has a high specific gravity and great power for refracting light. It has a splendid luster, and is used in the manufacture of cut glass, the engraving being done by means of a sand-blast. *Strass*, a variety of glass, is richer in lead than is flint glass, and on account of its fine luster finds use in the production of artificial gems.

Lead-soda glass is employed in the manufacture of electric-light bulbs.

Glasses are regarded as supercooled liquids, or liquids of great viscosity. When a glass is heated, it gradually softens and has, therefore, no sharp melting point as has a crystalline solid, such as silver, ice, or salt. Some chemists regard glass as a homogeneous solution of silicates. Glass is an amorphous body, but on being kept for some time at a temperature insufficient to render it fluid, "devitrification" occurs, *i.e.*, some of the components crystallize out.

Glass is produced by heating the raw materials to fusion in a furnace. The materials are contained in carefully made clay pots, which must be capable of sustaining a temperature of about $1,350^\circ$ to over $1,600^\circ \text{C}$. for nearly twenty-four hours. Potmaking for glass is done by hand and foot. The clay is kneaded by the bare feet of the workmen, and the pots are built up by hand, layer by layer, until all air-holes and cracks have been eliminated.

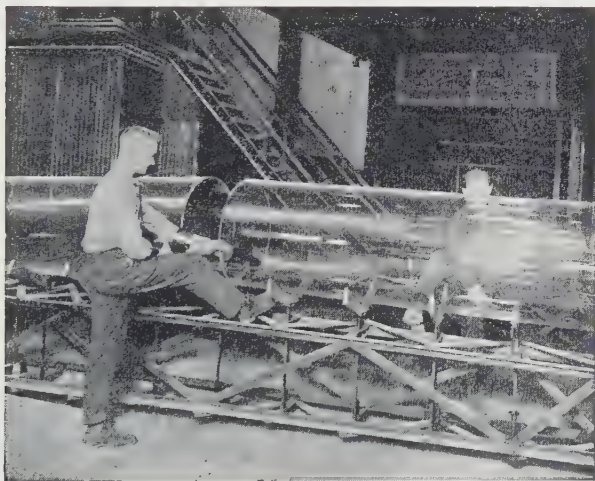
Glass is blown and fashioned into many different objects. For instance, in the production of window-panes the workman takes a mass of soft glass on the end of a long iron blowpipe and blows it into a large bubble. It is then drawn out into a cylinder, the ends are cut off, and the cylinder split lengthwise, then spread upon a plate. Plate glass may be rolled by means of hot cylin-



Courtesy, Pittsburgh Plate Glass Co.

FIG. 147. Blowing Glass Cylinders by Machinery.

ders. The thick glass is poured upon water-cooled metal tables and rolled out by heavy steel rollers. The drawing of window-glass cylinders is now done by machinery. When the cylinders have reached a length of about forty feet, they are lowered, flattened out, and cut into panes (Figs. 147 and 148). Bottles and electric-light bulbs also are blown by great machines, which are almost lifelike in their performance, one machine doing the work of a very large number of men. Glass-blowing machines



Courtesy, Pittsburgh Plate Glass Co.

FIG. 148. Dividing the Cylinders.

are a great boon, for tuberculosis is the scourge of the glass-blower's trade. The mortality in this branch of labor has been materially reduced since the introduction of glass-blowing machines. The first fully automatic bottle-machine was invented in 1903 by J. Owens, an American.

Plate glass is now manufactured by a revolutionary method. The glass is cast in a continuous unbroken sheet. Molten glass flows in a stream onto a revolving drum and passes under a roller which forms it into a sheet. The sheet then passes to the lehr, or annealing oven. A slowly moving sheet of glass, hundreds of feet long, is cooled from about 750°C. to a temperature cold enough to handle. At the end of the lehr the long sheet of glass is cut into sections and then ground and polished.

Glass may be colored by adding small quantities of certain foreign

substances. Thus, an exceedingly small quantity of cobalt oxide colors glass blue; chromium oxide, green; manganese dioxide, violet; sulfur, carbonaceous matters, silver or uranium oxide, yellow or amber; selenium (as a selenate with a reducing agent), orange; metallic gold or copper, cuprous oxide or selenium oxide, red. Ferrous iron colors glass green (bottle glass), while ferric iron colors it yellow or brown. The green color of common glass may be changed to the less objectionable yellowish tint by the addition of manganese dioxide. During the recent war the supply of pyrolusite from Brazil was cut off, due to the lack of ships; therefore selenium was temporarily substituted for manganese as a decolorizer of glass. The color of glass is generally due to the presence of colored silicates. The ruby-red color of the glasses made by the addition of gold or copper is caused by the metal in colloidal dispersion. Sulfur produces sodium or potassium sulfides, which color the glass. White, "opal," or "milk" glass is produced by adding cryolite, fluorite, bone-ash, or tin oxide, with feldspar. Black glass is produced by adding a large quantity of manganese dioxide, or of iron or copper oxides. Perfectly transparent colorless glass was apparently unknown to the ancients.

The art of manufacturing glass is very old. The early Egyptians were familiar with it, for glass beads have been found in mummy cases at least 3,000 years old. Glass articles also have been discovered in the excavations of Nineveh. Venice was formerly the center of the industry, but was finally displaced by Bohemia. The Bohemians produced fine crystal glass, and invented the art of engraving on it. Great quantities of glass are manufactured in England, France, Germany, the United States, Belgium, and Austria. Belgium and England have been particularly noted for window and plate glass, and Austria and Germany for blown ware.

Before the Great War, the United States imported from Germany nearly all the glass used in the manufacture of optical instruments. When the foreign supply of optical glass was cut off, our scientists and manufacturers undertook to work out the problem of producing this variety of glass, and before the end of the war our supply was in excess of the needs.

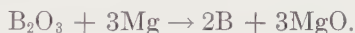
Optical glasses were produced at an early date. In 1303, Gui de Chauliac, a French surgeon, recommended the use of spectacles. Optical glass is of the highest importance, but is difficult to produce.

BORON. B = 10.82

463. History and Occurrence. — Boron is never found in the free state; its chief natural compound is borax, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, which has been known for centuries. Impure borax, known as *tincal*, was formerly exported from Tibet. Other important naturally-occurring compounds of boron are *boric acid*, H_3BO_3 ;

colemanite, $\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$; and *boracite*, $2\text{Mg}_3\text{B}_3\text{O}_{15} \cdot \text{MgCl}_2$. A rich deposit of a new boron mineral was discovered by C. M. Rasor in California, in 1926; it is called *rasorite* or *kernite*. The presence of boric acid or its salts has been detected in sea-water. It is said to exist in nearly all fruits. The element boron was first prepared independently by Gay-Lussac and Thénard and by Davy, about 1808, by the reduction of boron trioxide with potassium. Boric acid was first prepared from borax by Homberg in 1702.

464. **Preparation.** — Boron may be prepared by heating boron trioxide with magnesium (Moissan):



The magnesium oxide may be dissolved in hydrochloric acid, leaving boron as an amorphous brown powder. Sodium or potassium may be substituted for magnesium. Boron thus prepared is not pure. By heating B_2O_3 with excess of powdered aluminium, crystals of boron containing aluminium are found in the solidified mass. The metal may be dissolved in dilute hydrochloric acid.

Boron in the purest state is prepared by reducing boron trichloride with hydrogen in the high-tension electric arc (Weintraub):



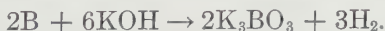
465. **Properties.** — Amorphous boron is a dark-brown powder of sp. gr. 2.45; its melting point is above $2,200^\circ$, and it is a poor conductor at ordinary temperatures. At 400° its conductivity for electricity is over 2,000,000 times that at ordinary room temperature. Metals, however, are better conductors at low than at high temperatures.

Boron is an active element at high temperatures; it burns in air at 700° to form B_2O_3 and BN. Boron unites directly with fluorine, chlorine, and bromine. At the temperature of the electric arc it combines with carbon to form a carbide, B_6C , which stands next to the diamond in hardness.

Hot concentrated nitric acid oxidizes boron to boric acid:



On fusion with caustic alkalies, a borate is formed:



The crystalline form of boron has a sp. gr. of 2.68, and is hard enough to scratch both ruby and corundum; it is more resistant to the action of reagents than is amorphous boron. The luster and hardness of crystalline boron are near that of the diamond.

Boron can be alloyed with iron or steel, such alloys being very hard, but they have no industrial use at present.

Boron suboxide or boron carbide will reduce cuprous oxide in molten copper, and will not alloy with the copper. Cast copper of high conductivity can therefore be produced by the use of these deoxidizers.

The most important compounds of boron are *boric acid* and *borax*.

466. **Boric Acid, H_3BO_3 .** — *Boric acid*, or *orthoboric acid*, has been obtained for about a hundred years from the waters or steam of volcanic regions in Tuscany. The jets of steam and hot gases, called *soffioni*, which issue from cracks in the ground in these extensive and desolate regions, contain small quantities (usually less than 0.1 per cent) of boric acid. Boric acid is obtained by surrounding the steam jets by basins, which are usually built on the side of a hill. The vapors are condensed in these basins, and the liquid is finally concentrated in lead-lined pans which are heated by the gases from the soffioni.

When the concentrated liquid is allowed to cool, impure boric acid crystallizes out. The acid may be purified by recrystallization. The Tuscan lagoons supply the European market with much of the boric acid.

Boric acid also is prepared by treating sodium tetraborate (borax) with hydrochloric or sulfuric acid:



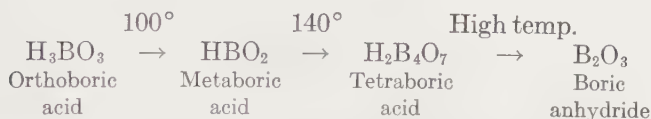
Boric acid is a white crystalline substance, which separates from aqueous solution in thin, lustrous flakes, belonging to the triclinic system, which are greasy to the touch. It is sparingly soluble in cold water, but quite soluble in hot water. At 20°, about 4 g. of H_3BO_3 dissolve in 100 g. of water, and at 100°, 28.7 parts.

Boric acid is a feeble acid, its aqueous solution being a poor conductor of electricity and turning litmus a wine-red color (see Carbonic Acid). It behaves as a monobasic acid, ionizing thus:



On the other hand, boric acid forms an ethyl ester (760), $B(OC_2H_5)_3$,

which indicates that it is a tribasic acid, $B(OH)_3$. When its aqueous solution is boiled, boric acid volatilizes with the steam, which explains the presence of the acid in the soffioni of Tuscany. When H_3BO_3 is heated, it loses water, finally forming the anhydride B_2O_3 :



These dehydrated compounds interact with water to form orthoboric acid:



Boric anhydride is not volatile below a white heat. It expels more volatile anhydrides from their salts. Thus, when K_2SO_4 is heated with B_2O_3 , SO_3 is expelled, and potassium borate is formed.

When boric acid is heated with alcohol, the vapor burns with a fine green flame — a delicate test for the acid. A solution of boric acid, or a borate acidified with hydrochloric acid, turns turmeric paper reddish brown, particularly when the paper is dried. When an alkali is brought in contact with the paper, it turns dark. This is a very sensitive test for boric acid. Boric acid is used extensively as an antiseptic and preservative, but it is only a mild antiseptic. When a powerful antiseptic such as corrosive sublimate or carbolic acid has been used, boric acid may be applied to maintain the aseptic condition.

A half-saturated solution (2 per cent) is used in medicine as an eye-wash, etc., and is known as *boracic acid*. The use of boric acid as a preservative for foods is prohibited in certain states. Boric acid also is used in the manufacture of enamels and glazes for pottery.

467. Borates. — Salts of orthoboric acid are practically unknown, the only one which is known with certainty being $Mg_3(BO_3)_2$. Metaborates, however, are well known. The best known salt containing boron is **sodium tetraborate** (pyroborate) or **borax**, $Na_2B_4O_7 \cdot 10H_2O$, which occurs in California, in Ceylon, and in Tibet.

In Germany (Stassfurt deposits) *boracite* (463) occurs abundantly, and borax is manufactured by decomposing the mineral with hydrochloric acid, and then treating the acid with sodium carbonate:



The mineral *ulexite* ($\text{NaCaB}_5\text{O}_7 \cdot 8\text{H}_2\text{O}$) occurs abundantly in California and in Nevada, and is used in the manufacture of borax and boric acid.

Kernite (rasorite) is abundant in the Mohave Desert, California. The deposit lies 300–400 feet below the surface, is more than 100 feet thick, and extends 500 feet or more in every direction. This mineral was discovered in 1926 and mining began the following year. Kernite is a form of sodium tetraborate, having the formula $\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$. As mined, it contains about 25 per cent of clay. It is readily purified by dissolving in water, filtering off the clay, and then allowing recrystallization to take place. The product is borax, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, which is considerably heavier than the tetrahydrate.

Before the discovery of kernite, the world's supply of borax was derived chiefly from the minerals ulexite, colemanite, and borax. In Italy it was produced by utilizing volcanic steam containing boric acid.

Borax is recovered from the brines of Searles Lake. Due to recent investigations on the processes of production of borax, the price of the compound has been greatly reduced. Borax which sold for 150 dollars a ton in 1920 sold for 50 dollars a ton in 1928.

When borax is crystallized from water at ordinary temperatures, it has the formula $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$; but at or above 56° , it is $\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$. The decahydrate crystallizes in the monoclinic system, while the pentahydrate is octahedral.

Borax is soluble in water and being a salt of a strong base and a feeble acid, it hydrolyzes partially, giving an alkaline reaction. Borax is stable at high temperatures.

Borax is used in the form of beads in analysis. (See Sodium Metaphosphate.) The formula of the compound may be written $2\text{NaBO}_2 \cdot \text{B}_2\text{O}_3$, in which there is an excess of the acid anhydride. When borax is fused with oxides of metals, a mixed metaborate may be formed. In case cobalt oxide (CoO) is employed, a blue bead, $2\text{NaBO}_2 \cdot \text{Co}(\text{BO}_2)_2$, is formed.

Borax is also used in hard soldering, welding iron, in the manufacture of glazes, enamels and soaps, in the laundry, in degumming silk, for preserving meat, etc.

Borax is a very useful flux, *i.e.*, it converts substances infusible at certain temperatures into other substances which melt; hence its use in metallurgy.

Borax is used in the manufacture of heat-resisting glass. Solu-

tions of borax have a hydrogen-ion concentration approximating that of neutral soap, and borax is more suitable for use as a mildly alkaline buffer than are the modified sodas ordinarily used.

468. **Review and Supplementary.** — In our study of the non-metallic elements we have seen that ordinary oxygen, hydrogen, nitrogen, and the gases of the helium family are colorless, odorless, tasteless gases, difficultly liquefiable, and but slightly soluble in water. The elements of the halogen family possess both color and odor. Fluorine and chlorine are greenish-yellow gases, bromine is a heavy dark-red liquid, while iodine is a heavy steel-gray solid, which forms a violet vapor when heated. The other non-metals are solids which vary widely in physical properties, such as hardness and melting points. Some of them, such as silicon and tellurium, have the appearance of metals, but they do not possess malleability and ductility. Phosphorus and sulfur are soft; but carbon, silicon, and boron are exceedingly hard.

Many of the non-metals exhibit allotropy: for example, oxygen, hydrogen, nitrogen, the elements of the sulfur family, phosphorus, carbon, and silicon.

In their chemical activity the non-metals show the widest variation. Thus, phosphorus catches fire spontaneously, while the elements of the helium family show practically no tendency to form compounds.

Most of the non-metals form *hydrides*, such as:



The halides of hydrogen are colorless gases, and dissolve in water to form important acids:



The *oxides* of the non-metals are numerous, but no oxides of fluorine or of bromine are known. Water, H_2O , is neutral and practically non-ionized; hydrogen peroxide, H_2O_2 , is a feeble acid; while many of the other oxides are acidic anhydrides: for instance, SO_2 , SO_3 , N_2O_3 , N_2O_5 , P_2O_3 , P_2O_5 , CO_2 , SiO_2 , and B_2O_3 . These oxides interact, in general, with water to form such acids as the following, in which the non-metal is a constituent of the anion:



The acids of a particular non-metal like nitrogen or sulfur increase in strength or activity with increase of percentage of

oxygen. Thus, HNO_3 is stronger than HNO_2 , and H_2SO_4 than H_2SO_3 .

Many oxygen compounds are analogous to sulfur compounds:

H_2O	CO_2	NaOH	As_2O_3	As_2O_5	H_3AsO_4
H_2S	CS_2	NaSH	As_2S_3	As_2S_5	H_3AsS_4

For the purpose of analysis, acids may be divided into groups which are based upon the solubility of their barium and silver salts. The reactions are carried out in neutral solution with the two reagents barium chloride (BaCl_2) and silver nitrate (AgNO_3). The groups are as follows:

(I) **The Nitrate Group.** *This group contains acids which do not yield a precipitate with either reagent. It includes the following acids:*

Nitric, HNO_3
 Chloric, HClO_3
 Acetic, $\text{H}(\text{C}_2\text{H}_3\text{O}_2)$
 Nitrous, HNO_2 .

These acids have scarcely any insoluble salts.

(II) **The Sulfate Group.** *The acids of this group yield precipitates with BaCl_2 , but not with AgNO_3 . They are —*

Sulfuric, H_2SO_4 , and
 Hydrofluoric, H_2F_2 .

The barium salts are insoluble in acetic acid.

(III) **The Chloride Group.** *These acids yield precipitates with AgNO_3 , but not with BaCl_2 . Among the acids in this group are —*

Hydrochloric, HCl	} (Silver salts readily soluble in dilute NH_4OH .)
Hydrocyanic, HCN	
Hypochlorous, HClO	
Thiocyanic, HCNS	(Silver salt difficultly soluble in NH_4OH .)
Hydrobromic, HBr	} (Silver salts practically insoluble in dilute NH_4OH .)
Hydriodic, HI	
Hydrosulfuric, H_2S	

(IV) **The Carbonate Group.** *These acids yield precipitates with both BaCl_2 and AgNO_3 . Practically all the salts of these acids are insoluble in water, save those of the alkali metals. Some of the common acids in this group are the following:*

Carbonic, H_2CO_3
 Sulfurous, H_2SO_3
 Boric, H_3BO_3
 Metasilicic, H_2SiO_3
 Phosphoric, H_3PO_4

Arsenious, H_3AsO_3
 Arsenic, H_3AsO_4
 Oxalic, $\text{H}_2\text{C}_2\text{O}_4$
 Fluosilicic, H_2SiF_6 .

EXERCISES

1. Compare and contrast silicon and its compounds with carbon and its compounds.
2. Show the relation of boron to silicon.
3. Contrast the rôle of silicon dioxide in nature with that of carbon dioxide. Compare and contrast the properties of the oxides.
4. How may pure boron and silicon be prepared?
5. How is ferrosilicon manufactured? Write the equation to show the action of sodium hydroxide upon ferrosilicon, assuming that its composition may be represented by the formula FeSi .
6. How large a balloon could be filled with hydrogen, measured at 20° and 770 mm., by treating with sodium hydroxide 100 kilograms of ferrosilicon containing 31.9 per cent of silicon?
7. How is silicon chloride manufactured? Explain the use of the compound during the Great War. Contrast the properties of silicon chloride and silicon fluoride.
8. How is transparent quartz produced and what are its properties?
9. Outline the manufacture of water glass. For what is water glass used? Explain.
10. Discuss the oxyacids of silicon. Explain what is meant by polysilicic acids.
11. Give names and formulae of a number of important silicates found in nature. State some of their uses. What is granite? asbestos? trap rock?
12. How would you treat feldspar or kaolin so as to render it soluble?
13. What did Graham mean by colloids and crystalloids? Describe his method of dialysis.
14. How would you obtain silicic acid as a hydrogel and as a hydrosol?
15. What are glasses? Give proof that glass is not a true solid. Give the approximate composition of the three classes of glasses. How are glasses colored? How would you produce blue, green, amethyst, red, yellow, and "milk" glass? How may the green color of common glass be destroyed?
16. Outline two methods for manufacturing boric acid. State its properties and uses. Give two tests for the acid.
17. Give the sources and preparation of borax. Explain its use in analysis, in metallurgy, etc. What is a flux?
18. Compare the allotropic forms of carbon and silicon.
19. Explain the action of heat upon boric acid and upon the acids of silicon.
20. Cite evidence to show that boric acid and silicic acid are feeble. How do they compare in strength with carbonic acid?
21. Into what four groups are acids usually divided for purpose of analysis? Explain, and illustrate by giving examples in each group.

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CHAPTER XXVI

COLLOID CHEMISTRY

469. **Introductory.** — We have seen that “true” solutions not only pass through filters, but ordinarily remain perfectly dark when a beam of light is passed through them (161). This means that the individual particles of the solute, *e.g.*, sugar, are intimately mixed with the particles of the solvent, or the component substances of the solution have become molecularly dispersed in each other. We also have seen that matter may assume a state of subdivision which is intermediate between true solution and ordinary dispersion or suspension. Matter in this state of subdivision is said to be in

colloidal solution (or suspension). A colloidal solution passes through an ordinary filter, but when a powerful beam of light in a darkened room is passed through it, the

presence of highly dispersed particles is revealed, the visibility of the beam being due to the scattering effect of the minute particles (perhaps aggregates of molecules). This is known as the *Tyndall phenomenon*.

This phenomenon is illustrated by Fig. 149, in which *C* is the vessel containing the colloidal solution, *LL* the beam of light, and *M* the microscope for observing the path of the ray.

As stated before (458), Graham divided bodies into two classes — *crystalloids* and *colloids*. The former include substances such as salt, sugar, and copper sulfate, which are crystalline, and the latter such substances as starch, silicic acid, glue and gums, which do not exhibit crystalline forms. Graham also invented a method called **dialysis**, which is employed to separate crystalloids from colloids. Experiment has shown, however, that no sharp line can be drawn between colloids and crystalloids. It is probable that all substances can appear as colloids under appropriate

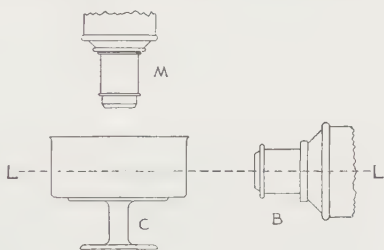


FIG. 149.

conditions; therefore it is now customary to speak of "a colloidal state instead of a colloidal substance." Common salt, for example, crystallizes in the isometric system, but it is possible to disperse salt in petroleum ether so that it exhibits the colloidal state. A colloidal substance may therefore be crystalline. According to Bancroft, "we call any phase (3) colloidal when it is sufficiently finely divided or dispersed. . . . Colloid chemistry is the chemistry of bubbles, drops, grains, filaments, and films, because in each of these cases at least one dimension of the phase is very small."

Colloid chemistry is, therefore, primarily a matter of size of particles; it is the chemistry of very small particles.

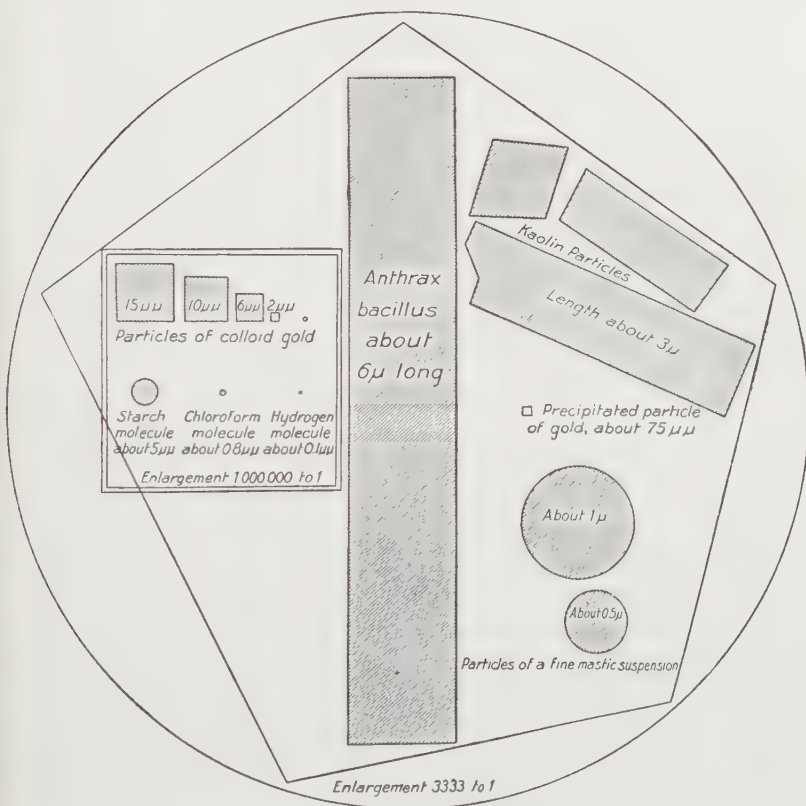
Since colloid chemistry is the chemistry of bubbles, drops, grains, filaments, and films, it is closely connected with everyday life. A knowledge of this branch of chemistry is necessary in order to understand the following, as well as innumerable other things: Milk, cream, butter, and cheese; fog and mist; smoke and fine dust; froth and foam; cooking, washing, and dyeing; soap, greases, and oils; photography; living matter; blood serum; the sap of plants; the principal articles of food; rubber and gums; clay, cements, ceramics; asphalt and roads; etc.

470. Dispersoids. — The diameters of particles vary within wide limits and may be expressed in *microns* or in *millimicrons*,¹ or *submicrons*. Particles having a diameter greater than 1μ are in coarse suspension and may be filtered out; while particles dispersed or scattered in a liquid and having diameters less than $20\mu\mu$ do not settle at all.

The best microscope does not reveal particles having a diameter less than about $1/2,000$ millimeter (0.5μ). Colloidal particles are still smaller. In 1903, Siedentopf and Zsigmondy invented an instrument known as the **ultramicroscope**, which reveals particles having a diameter of as small as $1/100,000$ millimeter ($10\mu\mu$). This instrument involves the same principle as the Tyndall phenomenon. In the ultramicroscope a converging beam of intense light in a darkened room is sent horizontally through the liquid under examination and the place where the light is brought to a focus is viewed from above, through an ordinary microscope. In the ultramicroscope, therefore, ultra-illumination is employed. But H. Freundlich says, "we must not infer the absence of colloidal particles from the failure of the ultramicroscope to reveal

¹ The symbol μ is used for a micron and $\mu\mu$ for a millimicron. The micron equals 0.001 millimeter; the millimicron, 0.000001 millimeter.

them." According to him, with the aid of the ultramicroscope it has been possible to demonstrate in many colloidal solutions particles having a diameter from $10\mu\mu$ – $500\mu\mu$. He also states



Courtesy, P. Blakiston's Son and Co.

FIG. 150. Comparison of Particles of Different Size. (From "Handbook of Colloid Chemistry" by Ostwald-Fischer.)

that the diameters of colloidal particles range from $1\mu\mu$ to $500\mu\mu$. In the case of true solutions it may be assumed in general that the particles have diameters less than $1\mu\mu$, which means that they are of molecular dimensions.

The sizes of a number of particles are approximately as follows (Fig. 150):

	<i>Diameter</i>
Hydrogen molecule.....	0.1 $\mu\mu$
Water vapor molecule.....	0.1 "
Common salt molecule.....	0.26 "
Sugar molecule.....	0.7 "
Particles of colloid gold.....	2-15 "
Particles of precipitated gold.....	75 "
Starch molecule.....	5 "
Red-blood corpuscle.....	7.5 μ

The length of the anthrax bacillus is about six microns. The sizes of the blood corpuscles and of the anthrax bacillus are very large as compared with those of molecules and colloidal particles.

The finely divided discontinuous phase is called the *disperse phase*, or *internal phase*; the other continuous phase (external phase) is called the *dispersion means*. Thus, in the case of colloidal arsenic trisulfide, As_2S_3 is the disperse phase (internal phase) and water the dispersion means, or external phase.

Dispersoids may therefore be classified as follows:

(1) **True or Coarse Dispersions.** Size of particles of the disperse phase greater than $10\mu\mu$. Under this head we have (a) suspensions and (b) emulsions.

(2) **Colloid Solutions.** Size of the particles of the disperse phase between $1\mu\mu$ and $500\mu\mu$.

(3) **Molecular and Supermolecular Dispersoids.** Size of particles of the disperse phase about $1\mu\mu$ or less. True solutions come under this head.

471. Properties of Colloids. — The principal *characteristics of colloids* are as follows:

(1) *The freezing points and boiling points of colloidal solutions differ but little, if any, from those of the dispersion means (e.g., water).* The physical properties of true solutions, however, are greatly influenced by the solute. Furthermore, colloids diffuse slowly. According to Graham, colloids have a much lower rate of diffusion than crystalloids. Diffusion is closely connected with dialysis. Crystalloids pass through parchment paper and animal membranes more or less readily, while colloids, as a rule, have but little tendency to diffuse, or to pass through membranes.

(2) *Colloidal solutions exhibit the Tyndall phenomenon.* True solutions (molecular-disperse solutions) do not exhibit definite Tyndall light-cones, or show them only in high concentration. This optical difference is one of the best ways to differentiate a true solution from a colloidal solution. *Colloidal solutions show the Brownian movement (60).*

472. **Theory of Colloidal Suspension and Coagulation.** — Why do colloidal particles remain in suspension? There are at least three reasons:

(1) *Colloidal particles carry electrical charges:* for instance, particles of colloidal ferric hydroxide are positively charged, while particles of colloidal arsenic trisulfide are negatively charged. Particles carrying the same kind of charge repel one another, thus preventing the matter from settling. If this theory be true, the charged particles should move or migrate when an electric current is passed into a colloidal solution. There are plenty of illustrations of this kind, the phenomenon being known as **cata-phoresis** (Greek, *down + bearing*). This process may be illustrated by means of milk, in which the fat-globules are negatively charged and should therefore migrate or travel to the positive electrode, or anode, under the influence of the electric current. The milk is poured into a U-tube, and a layer of water is carefully introduced above the milk in both limbs of the tube. Platinum electrodes are now immersed in the water, and a potential difference of about one hundred volts is set up between the electrodes. In the course of time it may be observed that the fat globules are moving toward the anode and away from the cathode.

(2) *Colloidal solutions exhibit the Brownian movement*, while true solutions do not. The particles of the colloid are suspended in the dispersion means (ordinarily water), and are subjected to lively bombardment by the molecules of the liquid, and are thus kept in a state of perpetual motion. When viewed through the ultramicroscope, this phenomenon is most interesting. The colloidal particles are not actually visible, but one sees the light diffracted by them. This phenomenon may be compared to motes dancing in a beam of sunlight.

(3) *Settling may be prevented by the presence of protecting films.* When Faraday prepared colloidal gold in 1857 he observed that a little jelly kept his preparations from coagulating. The action of gelatin in preventing coagulation is of much interest and importance. This fact can be well illustrated by the following experiment:

Prepare a colloidal solution of gelatin by adding 1 g. of the substance to 100 cubic centimeters of warm water. Cool the solution, add a few drops of concentrated hydrochloric acid, shake, and then add an excess of a solution of silver nitrate. Shake the tube and allow it to stand. The resulting substance is known as colloidal silver chloride. The chloride remains in suspension. But when a solution of silver nitrate is treated with hydrochloric

acid, gelatin being absent, a heavy, curdy precipitate of silver chloride is formed at once.

Colloidal silver bromide and iodide may also be prepared. The emulsions of the halides of silver are of great importance in photography.

It is believed that the liquid emulsoid particles cover the solid suspensoid particles, thus preventing their coming together to form larger aggregates. Such organic colloids as gelatin and the proteins increase the stability of colloidal metals; hence they are termed protective colloids.

In general, colloids may be coagulated by adding an electrolyte: e.g., hydrochloric acid or a solution of barium chloride will coagulate colloidal arsenic trisulfide. The electric charges (negative) of the sulfide are neutralized by the positive charges of the cations. Again, when a colloidal solution of arsenic trisulfide (negative) is mixed with one of ferric hydroxide (positive), precipitation occurs, for the oppositely charged particles neutralize one another. The casein of milk may be coagulated by adding acetic acid.

473. Preparation of Colloids. — The methods employed in the preparation of colloidal solutions can be divided into two classes — condensation methods and dispersion methods.

CONDENSATION METHODS

(1) **Reduction without Electrolysis.** To illustrate, colloidal gold can be prepared from dilute solutions of gold salts by reduction. Various reducing agents may be employed, such as formaldehyde and hydrazine. *Zsigmondy's gold* is prepared by reducing a solution of gold chloride ($\text{AuCl}_3 \cdot \text{HCl} \cdot 3\text{H}_2\text{O}$) with formaldehyde in the presence of potassium carbonate.

It is an interesting fact that Michael Faraday prepared violet and purple colloidal solutions of gold in 1857 by treating very dilute solutions of gold chloride with a solution of phosphorus in ether. Some of Faraday's specimens are preserved at the Royal Institution in London, one or two specimens still retaining a tinge of color, the rest having coagulated. Faraday's gold is an illustration of the preparation of a colloidal solution by chemical means.

Colloidal gold of different colors, such as red, blue, and violet, may be prepared, the color depending more or less upon the size of the particles.

(2) **Reduction with Electrolysis.** When very dilute solutions of the noble metals are subjected to electrolysis, some of the metal appears in the colloidal condition. Colloidal solutions of

certain of the less noble metals have also been prepared by this method.

(3) **Hydrolysis.** As an example, colloidal ferric hydroxide can be prepared by boiling a very dilute solution of ferric chloride:



(4) **Double Decomposition.** Thus, colloidal arsenic trisulfide is prepared by the interaction of arsenic trioxide (or arsenious acid) and hydrogen sulfide:



Colloidal arsenic trisulfide may be prepared as follows: Add 1 g. of As_2O_3 to 100 cc. of water, heat to boiling, shake thoroughly, cool to room temperature, and then filter. Add to this solution an equal volume of fresh hydrogen sulfide water, which is prepared by dissolving washed H_2S in distilled water. The liquid should be yellow and should show no turbidity.

DISPERSION METHODS

(1) **Electrical Disintegration (Bredig's Arc Method).** When an arc is formed under water between two metal wires (*e.g.*, wires of gold), the metal suffers disintegration and assumes the colloidal state. Colloidal solutions of gold, platinum, palladium, iridium, and cadmium have been prepared by this method. The disintegration occurs chiefly at the cathode. A current at a voltage of 30 to 110 and of 5 to 10 amperes may be employed. A trace of alkali in the water gives better results. Since the metal first forms a vapor which condenses to colloidal particles, some writers place the Bredig method under Condensation Methods.

(2) **Peptization.** Peptization is the disintegration of a substance or body into colloidal particles by the action of an added agent, say, water or caustic soda. Thus, water is employed as a peptizing agent in "dissolving" gelatin or glue. As a matter of fact, these bodies do not form true solutions in water, but colloidal solutions. Again, silicic acid can be peptized by caustic soda.

In a similar manner colloidal solutions of glue, starch, and egg albumin may be prepared. Peptization is roughly analogous to digestion, in which pepsin plays a rôle. The cook often adds pectin to fruit-juice to bring about coagulation, or the formation of jelly. This is known as *pectization*, which is the converse of peptization.

(3) **Mechanical Disintegration.** Colloidal nickel, silica, tungsten, etc., can be prepared by grinding the substance until the particles are exceedingly fine. This method is not of much practical value.

(4) **Emulsification.** An **emulsion** consists of droplets of one liquid suspended in another. It is easy to prepare emulsions by shaking two immiscible liquids together: *e.g.*, water and kerosene. Such dispersions, however, are temporary, the emulsions quickly separating into their components. In order to preserve an emulsion, it is necessary to have present a third substance — an *emulsifying agent*. Mayonnaise dressing, for example, is an emulsion of vinegar and olive oil, with the yolk of an egg as emulsifying agent.

Emulsoids, such as water suspensions of gelatin, glue, starch paste, egg albumin, etc., after evaporation to dryness, are readily thrown into suspension again by the addition of the dispersion means, *i.e.*, they are reversible. When matter in the suspensoid state, however, is evaporated to dryness, or coagulated, it cannot be suspended again by the addition of the dispersion means, *i.e.*, it is irreversible.

474. **Sols and Gels: "Solidified Alcohol."** — The terms **sol** and **gel** are frequently used in the study of colloids. A colloidal solution is called a **sol** when the dispersed substance is sufficiently finely divided and under such conditions that coalescence and agglomeration are prevented. In case water is the dispersing liquid, the colloidal solution is known as a **hydrosol**. Colloidal gold is a good illustration of a hydrosol. On the other hand, when the colloidal particles agglomerate and precipitate, a **gel** is obtained. In case water is the dispersing liquid, the precipitate is called a **hydrogel**. The term **gel** includes jelly, such as fruit jelly. Sometimes there is difficulty in getting the jelly properly to form, as was stated before, but coalescence and agglomeration can be induced by the addition of *pectin*, a preparation which may be purchased. Pectin is present in ripe fruits, and the jelling of fruit-juices depends upon it. If the fruit is cooked too much, pectin is converted into other substances and the formation of jelly is prevented.

Solidified alcohol, which is so common nowadays, is essentially an alcoholic soap jelly.

A specimen of gel may be prepared by pouring 10 cc. of a saturated solution of calcium acetate into 90 cc. of 95 per cent alcohol. The two liquids should be contained in small beakers, and poured quickly back and forth until the

gel forms. Pieces of the gel may be ignited. This preparation was patented by C. Baskerville.

Silica gel is of great commercial significance, being known as "Patrick's silica gel." This gel is formed when sodium silicate of proper concentration (water glass) is treated with hydrochloric acid. It is broken into small pieces, washed, and dried. Silica gel is a hydrated form of silica (SiO_2). It is a hard, glass-like substance, and has great power for taking up or adsorbing water vapor and certain gases and liquids.

Many gels are largely water. They seem to have a regular structure of some kind, and possess a certain amount of rigidity and elasticity.

475. Adsorption and Gas-Masks. — In general, all solids have a tendency to condense upon their surfaces any gases or vapors with which they come in contact. This holding of substances on surfaces is called **adsorption**. Charcoal, for example, is a very porous substance and is therefore capable of adsorbing large volumes of ammonia and other gases. It is well known that coconut charcoal was employed in gas-masks during the late war to adsorb poisonous gases. Silica gel is also full of exceedingly fine capillaries and in consequence is able to adsorb enormous quantities of certain gases and liquids. It is a powerful drying agent, removes obnoxious sulfur compounds from crude petroleum, gasoline from casing-head gas, etc. Gas adsorption is now of great industrial importance. Animal charcoal is utilized extensively in the purification of sugar; it adsorbs the brown coloring matter.

A given mass of finely divided substance has a much larger surface than has the same mass in compact form. To illustrate, a cube of gold 1 centimeter on the edge has a surface of 6 square centimeters and weighs 19.32 g. If the cube could be divided into cubes $10\mu\mu$ on the edge (approximately the diameter of colloidal particles of bright red gold), the total surface would become 6,000,000 square centimeters and the total number of particles 10^{18} . If a cubic centimeter of gold could be divided into cubes having a length of edge of $0.001\mu\mu$ ($4/100,000,000,000$ inch), there would be 1 nonillion (1 followed by 30 ciphers) cubes, having a total surface of 1,482.6 acres, or $2\frac{1}{3}$ square miles! These dimensions of the tiny cubes are still a thousand times larger than the theoretical size of the electron. Charcoal, silica gel, and matter in the colloidal form have great adsorptive power, for they all possess very large surfaces in proportion to mass.

Solids not only adsorb gases and vapors, but they adsorb liquids and solids. Moreover, liquids may adsorb vapors, liquids, and solids. In fact, adsorption is a very broad term, and it plays a great rôle. Bacteria, for example, are removed from water by means of sand filters; they are small enough to pass between the particles of sand, but are adsorbed by, or held upon the surface of, the sand.

Salts used as fertilizers are adsorbed by the soil and not washed away by the rain. Adsorption also plays an important part in tanning. Skins are colloidal in nature, and they adsorb water to form gels in the processes preliminary to tanning. When the hides are tanned, the positively charged colloidal particles of the hide and the negatively charged particles of the colloid, tannin, mutually attract and coagulate each other, and chemical changes complete the formation of leather.

476. Classification. — Wolfgang Ostwald classifies colloids according to the physical state (gaseous, liquid, or solid) of the subdivided substance, or dispersed phase, and of the dispersion medium, *i.e.*, the medium in which the particles of the subdivided substance are distributed. These classes or groups of disperse systems are given below. G, L, and S stand for gas, liquid, and solid, respectively.

Example. —

- (1) G + G No example, for gases are miscible in all proportions.
- (2) G + L Fine foam, gas in beer.
- (3) G + S Gaseous inclusions in minerals, metals, etc.: *e.g.*, pumice, hydrogen in iron.
- (4) L + G Fog, clouds, gases at critical state.
- (5) L + L Emulsions, such as oil in water, cream, colloidal water in chloroform.
- (6) L + S Mercury in ointments, liquid inclusions in minerals.
- (7) S + G Cosmic dust, smoke, and condensing vapors.
- (8) S + L Colloidal gold, salt in petroleum ether.
- (9) S + S Solid solutions, such as colloidal gold in ruby glass, coloring matter in gems.

477. Applications of Colloid Chemistry. — As previously stated, the applications of this branch of chemistry are almost innumerable. One interesting application is to the precipitation of dust and smoke. F. G. Cottrell, an American chemist, perfected an industrial method which is called the **Cottrell process**. It is employed, for instance, in smelting-works, in cement-mills, and in sulfuric acid plants. The colloidal particles are precipitated by means of electrical forces. The dust or smoke is made to

pass by a charged point suspended in the center of a chimney or dust-chamber from the end of a high-voltage wire. The particles take on a charge similar to that of the point, whereupon they are attracted to a plate (or to the walls of the chimney or chamber) having the opposite charge, where they are precipitated. The plates or walls of the dust-collector are grounded. It was suggested by Sir Oliver Lodge that a ship might utilize the same principle in clearing its path of fog.

W. D. Bancroft and L. F. Warren scattered electrified sand by an airplane and succeeded in condensing moisture to fog and clouds, and even producing a slight localized "rain."

As a result of the violent volcanic eruption of Krakatau, August 26-27, 1883, fine particles were carried around the world and formed a layer from five to fifteen miles above the earth's surface.

Finely divided or colloidal clay is carried thousands of miles by the water of great rivers, and when it reaches the sea it is deposited as a result of the action of the ions of sea-salts, land being formed. According to geological evidence, this process has added about one thousand miles to the length of the Mississippi River and is still going on.

Colloidal fuel is now an article of commerce. It consists of finely powdered coal, cheap tars, and similar materials, dispersed in mineral oil and stabilized by means of a protective colloid, such as lime soap. This fuel is stored, piped, and burned, thus taking the place of oil.

Colloid chemistry also finds application in the *flotation process* (484).

The rubber-plant furnishes a milky juice, or latex, which contains very fine particles in colloidal solution. The latex may be coagulated by different processes, yielding a colloidal gel called rubber.

In 1839, Goodyear heated rubber with sulfur and obtained the product known as *vulcanized rubber*.

As stated before, particles in colloidal solution possess an electric charge, and under the influence of an electric current the particles move toward the electrode of opposite charge. A new process for the production of rubber goods is based upon an application of this principle.

The colloidal particles of the latex of rubber are negatively charged. When a mold or form is employed as anode in a properly prepared latex electrolytic solution and the circuit closed, the anode becomes rubber-plated. Molds of any form may be plated

with rubber of tissue-paper thinness to several inches in thickness. The rubber has great strength and resiliency. Bathing-caps, gloves, hot-water bottles, and many other articles may be manufactured by the new process. It is promising for insulating electric wires.

Many colored transparent glasses owe their color to colloidal dispersed particles: for example, colloidal particles of gold give a beautiful ruby glass.

An emulsion for killing San José scale and other parasites can be prepared from heavy mineral oil or lubricating oil. Very small quantities of the colloidal poisons suffice to kill insects.

Many natural phenomena can be explained in terms of colloid chemistry. The whiteness of the lily and of hair is due to numerous very small air bubbles. The color of certain blue feathers is believed to be due to innumerable air bubbles which fill the horny matter. The tail of a comet, which may have a length of millions of miles, is supposed to be made up of a vast cloud of colloiddally dispersed matter in a highly tenuous state; while its luminosity is a Tyndall effect on a vast scale, which may be compared to the beam of an automobile headlight or of a searchlight, which shoots through the atmosphere, especially if it is slightly hazy.

EXERCISES

1. How would you differentiate between a true solution and a colloidal solution? What is the Tyndall phenomenon? Compare it with a beam of bright light when passed through a darkened room.

2. Define and illustrate the following terms: (1) dispersoid; (2) electrophoresis; (3) protecting film; (4) hydrogel; (5) hydrosol.

3. What are the approximate limits as to the sizes of particles of coarse dispersions, colloid solutions, and true (molecular) solutions?

4. What is the ultramicroscope? Can one actually see colloidal particles by means of the ultramicroscope? Is it possible to estimate the size of colloidal particles, assuming that they are spherical and that their number and mass are known?

5. State, under three heads, the theory of colloidal suspensions. Explain and illustrate how colloids may be coagulated.

6. Outline and illustrate three condensation methods and three dispersion methods for preparing colloids.

7. Explain and illustrate the meaning of the terms peptization and emulsification. What is the difference between French dressing and mayonnaise dressing? What is the object of adding the yolk of an egg in preparing the latter?

8. What is meant by adsorption? Explain the use of charcoal as an adsorbent. How do sand filters remove bacteria from water? When rocks

containing potassium compounds disintegrate, why are not the potash salts carried into the sea? Explain the cleansing power of soap.

✓ 9. What type of ion is particularly effective in coagulating colloidal arsenic trisulfide? Why?

10. How may silica gel be prepared? State and explain some of its uses.

11. Explain the difference between peptization and pectization.

12. To what disperse systems do the following belong: (1) tobacco smoke; (2) foam; (3) milk; (4) ruby glass; (5) rain-clouds; (6) French dressing; (7) colloidal solution of silicic acid (hydrosol); (8) fog?

13. Outline some of the important applications of colloid chemistry, stating the principles involved.

14. Explain why an emulsifying agent stabilizes an emulsion.

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PART III
THE METALS

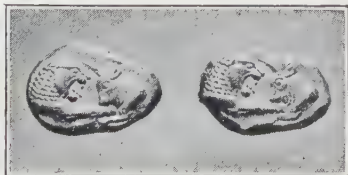
CHAPTER XXVII

THE METALLIC ELEMENTS — ALLOYS

478. **Metals and Non-metals.** — The elements have long been classed as *metals*, or *base-forming elements*, and as *non-metals*, or *acid-forming elements*. This classification is not ideal, for certain elements do not fall sharply into either class, *i.e.*, they possess both metallic and non-metallic characteristics, or are both basic and acidic in character: *e.g.*, arsenic and antimony. Such elements are sometimes called *metalloids*, or *amphoteric elements*.

The division of the elements into metals and non-metals is based upon their well-known physical properties. To illustrate, metals such as silver, iron, and copper possess physical properties very unlike those of such non-metals as nitrogen, chlorine, and sulfur. The typical metal is a lustrous, opaque, heavy, malleable, and ductile solid; while the typical non-metal is generally transparent and light, and lacking in mechanical properties such as malleability, ductility, and tensile strength.

479. **Historical.** — The metals known to the ancients were either those that occur native or may be obtained readily by reducing their ores. They are: *gold*, *silver*, *copper*, *lead*, *tin*, *iron*, and *mercury*. The use of gold and copper dates from pre-historic times, and it is probable that these were the first metals used by man. Both metals occur in the free state. As a rule, ancient gold is alloyed with silver, the latter metal having been known since at least 2,000 B.C. Gold coins nearly 2,500 years old have recently been found in the ruins of Sardis, the ancient capital of Lydia; some of them were coined during the reign of Croesus (Fig. 151). The manufacture of *bronze*, an alloy of copper and tin, dates from about 3,000 B.C. Copper and tin ores were reduced together to form the alloy, which is harder than copper. A



Courtesy, Dr. T. L. Shear.

FIG. 151. Gold Coins found at Sardis.

ring of tin has been discovered which dates from 1,450 B.C. *Brass*, an alloy of copper and zinc, has long been in use. The word was used indiscriminately in the Old Testament, both for copper and its alloys. The use of iron was no doubt later than that of gold and copper, for very little of the metal occurs in the native state. The Assyrians and the Egyptians, however, employed iron implements many centuries before the Christian Era. The word iron is mentioned in the Pentateuch, together with the furnaces in which it was prepared. Owing to its high melting point, iron is more difficult to work than copper. Lead is mentioned in the Book of Job and in the Book of Numbers. Pliny points out a distinction between lead and tin. Lead is rarely found native. It was used by the ancient Romans for water-pipes. Mercury was first described by Greek writers. Its ability to dissolve other metals, such as gold and silver, was known before our era. Nickel, cobalt, manganese, and platinum were discovered during the eighteenth century; but most of the remaining metals were first prepared during the nineteenth century.

480. Physical Characteristics of the Metals. — Metals possess certain physical characteristics which serve to differentiate them from non-metals:

(1) **Luster.** Metals in compact form possess, as a rule, a silvery luster. Gold and copper are conspicuous exceptions, the former having a yellow luster and the latter a red luster. In the finely divided state, however, a metal may be of a dark color or even black: *e.g.*, gold obtained by reducing a solution of gold trichloride with ferrous sulfate. Aluminium and magnesium, however, are silvery when finely divided. In colloidal form, a metal may exhibit various colors: *e.g.*, rose, red, violet, purple, blue, and green gold.

(2) **Density.** The densities of metals vary greatly, being in many cases greater than those of non-metals. The lightest known metal is lithium (density 0.53). Sodium and potassium are also light enough to float upon water. Other light metals are magnesium, aluminium, and the alkaline earth metals (Chap. XXX). Osmium has a density of 22.5, being the heaviest of the elements. Mercury has a density of 13.6, silver 10.5, and gold 19.3.

(3) **Melting Points.** The fusing points of metals also vary within very wide limits, ranging from -38.8° in the case of mercury to $3,400^{\circ}$ in the case of tungsten. The melting points of some of the metals are given on page 503.

Melting Points of Metals

Mercury.....	-38.8° C.	Barium.....	850.0° C.
Potassium.....	62.3 "	Arsenic.....	850.0 "
Sodium.....	97.5 "	Silver.....	960.5 "
Lithium.....	186.0 "	Gold.....	1063.0 "
Tin.....	232.0 "	Copper.....	1083.0 "
Bismuth.....	271.0 "	Manganese.....	1230.0 "
Cadmium.....	321.0 "	Beryllium.....	1350.0 "
Lead.....	327.0 "	Nickel.....	1452.0 "
Zinc.....	419.0 "	Cobalt.....	1480.0 "
Antimony.....	630.0 "	Iron.....	1530.0 "
Magnesium.....	651.0 "	Chromium.....	1615.0 "
Aluminium.....	659.0 "	Platinum.....	1755.0 "
Cadmium.....	810.0 "	Tungsten.....	3400.0 "

All the metals can be converted into vapor in the electric arc.

(4) **Malleability and Ductility.** Typical metals are malleable and ductile. Gold is the most malleable and ductile of metals. Gold has been hammered out into sheets so thin that it requires 280,000 leaves placed one upon another to occupy the thickness of an inch, and one ounce can be hammered out so as to cover 189 square feet. The thickness of the metal on gold lace is about 0.000002 mm. Gold is so ductile that 1 g. of it can be drawn into a wire 3,240 meters long.

The following groups show the order of malleability and ductility of a few of the metals:

Malleability

1. Gold	4. Aluminium	7. Lead
2. Silver	5. Tin	8. Zinc
3. Copper	6. Platinum	9. Iron

Ductility

1. Gold	4. Aluminium	7. Copper
2. Silver	5. Iron	8. Zinc
3. Platinum	6. Nickel	9. Tin

(5) **Tenacity.** In general, metals possess greater tenacity than non-metals. The tenacity is measured by the number of kilograms which a piece of the material one square millimeter in section can sustain without breaking. The following is the order of tenacity of a few common materials:

Tenacity

1. Steel	4. Copper	7. Zinc
2. Nickel	5. Aluminium	8. Tin
3. Iron	6. Gold	9. Lead

Metals combine great strength with a high degree of plasticity.

(6) **Hardness.** At ordinary temperatures mercury is a liquid, and sodium and potassium are so soft that they may be readily cut with a knife. On the other hand, iridium and chromium are hard enough to scratch glass.

(7) **Conductivity.** In general, metals are good conductors of electricity, although they vary much in this respect, silver conducting more than sixty times as well as mercury. Of the cheaper metals, copper is the best conductor, being nearly as good a conductor as silver. Aluminium has about two-thirds the conductivity of copper for equal diameter of wire. *The electrical conductivity of metals increases with fall in temperature, i.e., it varies inversely with the temperature.* When the more active metals, e.g., potassium, are exposed to ultra-violet light, electrons are given off from the surface of the metal, producing what is known as the *photoelectric effect*. When metals are heated, a similar phenomenon occurs. This fact is employed in the construction of the audion tubes of radio-telephony. Metals are good conductors of heat.

481. Chemical Properties of Metals. — The most important chemical characteristics of the metals are as follows:

(1) *Their oxides and hydroxides are basic.* For this reason the metals are called the base-forming elements. The oxide and hydroxide of calcium are typical:

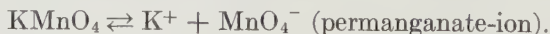


Certain metals form amphoteric hydroxides (see Zinc hydroxide and Aluminium hydroxide).

(2) *The metals form the positive radicals of salts, and when salts ionize the metals constitute the cations:*



Certain metallic elements also may be present in negative ions (anions): e.g., manganese in potassium permanganate:



(3) *The halide of a strongly basic metal is not hydrolyzed to any considerable extent: e.g., NaCl, KCl.* Cupric chloride, CuCl_2 , the salt of a less strongly basic element, is but slightly hydrolyzed. In the case of antimony and bismuth (weakly basic elements) the chlorides are partially hydrolyzed.

In general, the halides of non-metals are completely hydrolyzed: e.g., the halides of phosphorus (298).

482. **Occurrence.** — The more inactive metals occur in the free state, and are called *native*. Thus, gold and platinum occur largely in the native state; copper, silver, mercury, bismuth, arsenic, and antimony are also found free. A majority of the metals occur only in combination with another element or elements. *Ores* are minerals from which the useful metals are extracted: e.g., the mineral hematite (Fe_2O_3) is by far our most important ore of iron.

Some of the chief *minerals* containing metals are as follows:

Oxides

Ferric oxide, or Hematite	Fe_2O_3
Hydrated ferric oxide, or Limonite	$2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$
Magnetic oxide of iron, or Magnetite	Fe_3O_4
Stannic oxide, or Cassiterite	SnO_2
Zinc oxide, or Zincite	ZnO
Cuprous oxide, or Cuprite	Cu_2O
Manganese dioxide, or Pyrolusite	MnO_2
Aluminium oxide, or Bauxite	$\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$

Metals are obtained on a commercial scale by reducing these oxides.

Sulfides

Lead sulfide, or Galena	PbS
Zinc sulfide, or Sphalerite	ZnS
Iron disulfide, or Pyrite	FeS_2
Cuprous sulfide, or Chalcocite	Cu_2S
Antimony trisulfide, or Stibnite	Sb_2S_3
Mercuric sulfide, or Cinnabar	HgS
Silver sulfide, or Argentite	Ag_2S

Carbonates

Ferrous carbonate, or Siderite	FeCO_3
Zinc carbonate, or Smithsonite	ZnCO_3
Calcium carbonate, or Calcite	CaCO_3
Magnesium carbonate, or Magnesite	MgCO_3
Calcium magnesium carbonate, or Dolomite	$\text{CaMg}(\text{CO}_3)_2$
Strontium carbonate, or Strontianite	SrCO_3
Barium carbonate, or Witherite	BaCO_3
Basic copper carbonate, or Malachite	$\text{Cu}(\text{OH})_2 \cdot \text{CuCO}_3$

Sulfates

Calcium sulfate, or Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
Strontium sulfate, or Celestite	SrSO_4
Barium sulfate, or Barite	BaSO_4
Magnesium sulfate, or Epsomite	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$

Silicates

Aluminium silicate, or Kaolinite.....	$\text{Al}_2\text{H}_2(\text{SiO}_4)_2 \cdot \text{H}_2\text{O}$
Mica.....	$\text{KAl}_3\text{H}_2(\text{SiO}_4)_3$
Potash feldspar, or Orthoclase.....	KAlSi_3O_8
Magnesium hydrogen metasilicate, or Talc ...	$\text{Mg}_3\text{H}_2(\text{SiO}_3)_4$

Certain chlorides, such as NaCl, KCl, and MgCl_2 , are abundant also.

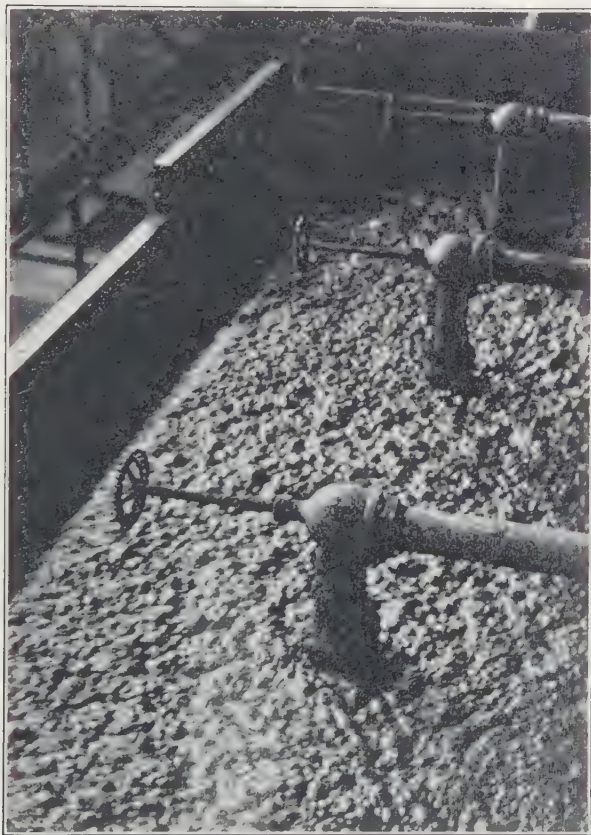
483. **Metallurgy.** — Metallurgy may be defined as “the science and art of preparing metals for use from their ores by separating them from mechanical mixture and chemical combination.”

It is often necessary to prepare an ore for metallurgical treatment, especially a low grade ore, by subjecting it to some process by which a large part of the gangue, or earthy matter, may be removed mechanically so as to lessen the cost of the subsequent metallurgical treatment, especially when the ore is to be smelted. Such treatment is generally termed “concentration,” and the products of the concentration process are termed “concentrates” and “tailings.” Concentrates are subsequently treated by a metallurgical process and the tailings, as a rule, go to waste.

Preparatory to concentrating an ore it is generally first crushed to a suitable size, screened and sized, and then passed over or through some form of apparatus, called a concentrator, by which the major portion of the gangue material is removed from the valuable metallic portions of the ore. This separation is usually effected by reason of the difference in specific gravity of the gangue and of the valuable portion of the ore, and for this reason such a process is known as the “wet gravity concentration process,” owing to the fact that separation is effected in water, and in such a concentration process the laws governing falling bodies in water are taken advantage of in order to increase the efficiency of the process and to effect the desired separation.

484. **The Oil Process of Ore Concentration: Flotation.** — In recent years the *oil process of ore concentration*, known as the *froth-flotation method*, has been used on a large scale, particularly for the concentration of low-grade sulfide ores, such as those of copper. Enormous quantities of ore are treated by this process in America. Finely ground ores or tailings, *e.g.*, tailings of copper ores, are agitated with water and a little oil. Metallic particles contained in the material treated, together with whatever gangue particles which have not been liberated from them by crushing, rise to the top with the oil, and the gangue sinks in the water (Fig. 152). The sulfide is preferentially wetted by the oil and

the gangue by the water. Each bubble is virtually armor-plated by a layer of ore particles. The froth can be removed mechanically. This is just the reverse of what happens in the gravity concentration process; that is, heavy metallic particles rise



Courtesy, The New Cornelia Copper Co.

FIG. 152. The Flotation Process.

instead of sinking. For this reason somebody has spoken of the oil-flotation process as being "gravity concentration upside down."

It is of interest to note that only a small quantity of oil is required. Not all oils are suitable. In America the so-called pine oil has been used extensively with or without admixture of

mineral oils. Eucalyptus oil has been used with success in Australia.

The ore must be of a metallic or semi-metallic character. In addition to the "oiling reagent," a "gangue modifying reagent" (usually alkalies or mineral acids) is employed. Air is introduced under such conditions that a stiff and lasting froth is produced, the oiled mineral particles adhering to the air-bubbles.

485. Divisions of Metallurgy. — At the present time there are two main divisions of metallurgy, namely, *pyrometallurgy* and *hydrometallurgy*. Some authors also add a division of electro-metallurgy. However, as the electric current is used either as a source of heat or for precipitating purposes, or for both simultaneously, as in the aluminium process, it can be regarded as an agent or reagent in either pyrometallurgical or hydrometallurgical work.

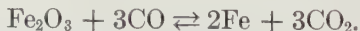
It was through the writings of Georgius Agricola (1494–1555) that the more important process of what we now term "pyrometallurgy" became known. Like his contemporary Paracelsus, Agricola was a physician. He was impelled to devote himself to mineralogy and metallurgy by the flourishing mining and smelting industry of Saxony.

In pyrometallurgical work, it may be stated, in general, that the ore containing more or less earthy matter, known as **matrix** or **gangue**, is heated with a **flux** which unites with the matrix to form a fusible **slag**. Thus, when hematite (Fe_2O_3) occurs mixed with silica (an acidic matrix), the latter is removed by heating the ore with limestone or lime (flux), the fusible slag calcium metasilicate being formed:



The following are the chief methods employed in **pyrometallurgy**:

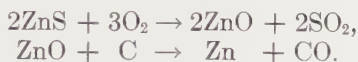
(1) **Reduction of oxides by carbon.** As a rule, the oxides of metals are reduced in an appropriate furnace by means of carbon (coke, coal, or charcoal). Thus, enormous quantities of coke are used in the metallurgy of iron. Some of the carbon is oxidized to carbon monoxide, which is also an important reducing agent:



When the ore is a carbonate or basic carbonate, it is first heated to obtain the oxide:



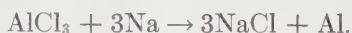
Sulfide ores are first roasted or calcined:



Large quantities of sulfur dioxide are obtained as a by-product in the smelting of sulfide ores; it is used in the manufacture of sulfuric acid, sulfites, etc.

Powdered coal is being used in smelting. It is blown into the furnace, and burns with a flame similar to that of a jet of gas (516).

(2) **Reduction by sodium, potassium, or magnesium.** Thus, aluminium has been prepared on a small scale by heating the chloride with sodium:



(3) **Reduction of oxides by hydrogen.** The oxides of metals from iron through gold lose oxygen when heated in the presence of hydrogen (126):



“Iron by hydrogen” is very finely divided and extremely active as compared with massive iron. This method is used in the laboratory.

(4) **Reduction by aluminium.** Finely divided aluminium has great affinity for oxygen; it will reduce oxides of most of the metals. In recent years this method has been employed to prepare such metals as chromium and manganese. Once the process is started, the reaction is exothermic. As a great quantity of heat is liberated, the process is called **aluminothermy**, and the mixture of oxide and aluminium is termed **thermite**. This method was first employed by the German chemist Goldschmidt. It

can be readily illustrated by reducing an oxide of iron, manganese, or chromium in a fire-clay crucible (Fig. 153). A mixture of the oxide and aluminium is introduced into a dry crucible, which is

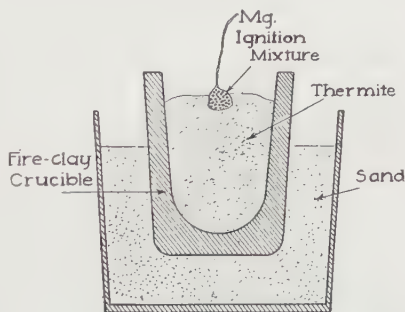


FIG. 153.

surrounded by sand. A small amount of a starting mixture (*e.g.*, barium peroxide and magnesium powder) is placed on top of the thermite, and this is ignited by means of a burning magnesium ribbon. As the reduction proceeds, more thermite may be added. The metal forms a regulus in the bottom of the crucible, the slag (Al_2O_3) collecting at the top:

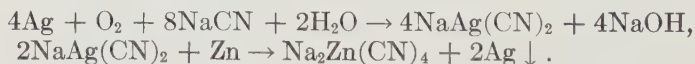


Owing to the great production of heat, the Goldschmidt process is used in welding.

The **hydrometallurgy** of a metal, according to Ralston,¹ consists in the preparation of the metal, or its compounds, through the medium of aqueous solutions of metallic compounds prepared from ores of metals or from other metallurgical products. In other words, the hydrometallurgy of metals, as ordinarily practiced, consists in dissolving the metal from its ores by proper chemical reagents, followed by recovery of the metal from solution by some suitable precipitating agent, or by electrolysis. For example, if copper is obtained in solution as sulfate, it can be precipitated as metallic copper by means of metallurgical iron, or by electrolyzing other solutions, as is done at Ajo, Arizona, at the plant of the New Cornelia Copper Company.

Hydrometallurgical processes are applied, as a rule, to ores which are too low in metallic content to permit of their being economically treated by a smelting process, and which likewise cannot be successfully concentrated into a product which will permit of being economically treated by a smelting process.

Gold and silver ores are treated with a solution of sodium or potassium cyanide, and the noble metal is obtained either by precipitation with a cheaper metal such as zinc, or by electrolysis of the complex cyanide:



The operation must be carried out in the presence of air, for oxygen is required. The cyanide process is very important.

Electrometallurgy is the department of metallurgy in which the electric current is employed not only for electrolytic separation or deposition of metals from solutions, but as a source of heat

¹ "Electrolytic Deposition and Hydrometallurgy of Zinc," by O. C. Ralston. McGraw-Hill Book Company, New York, 1921.

(electro-thermal process) in smelting, refining, annealing and welding. The use of the electric current is increasing: *e.g.*, sodium and potassium are manufactured by the electrolysis of the fused caustic alkalies, aluminium by the electrolysis of aluminium oxide dissolved in molten cryolite (582), and magnesium by the electrolysis of its oxide or chloride. Electrolytic zinc is produced by leaching the ore and then electrolyzing the solution with insoluble electrodes. There has been a great advance in leaching and direct electrolytic treatment of ores.

486. **Compounds of the Metals.** — The compounds containing metals are almost innumerable. The metals enter into the formation of salts, the number of which is very great. Salts may be formed by different methods (251). The properties of salts differ greatly. As a rule, their aqueous solutions are highly ionized and are good conductors of electricity. The general rules for the solubility of some common compounds containing metals are as follows:

GENERAL RULES FOR SOLUBILITY

<p>Compounds Soluble in Water: Compounds of Na, K, NH_4. All nitrates, chlorates, and acetates. The common halides.</p> <p>All sulfates.</p>	<p>Exceptions: Some basic nitrates and acetates are insoluble. Halides of Ag, Hg^+, and Pb (PbCl_2 is sparingly soluble in cold water and moderately soluble in hot water.) Certain fluorides, and sulfates of Ba, Sr, Ca, and Pb (calcium sulfate and strontium sulfate are slightly soluble).</p>
<p>Insoluble in Water, Soluble in Acids: All carbonates and phosphates.</p> <p>All oxides and hydroxides.</p>	<p>The salts of Na, K, and NH_4 are soluble. Those of Na, K, NH_4, Ca, Sr, and Ba are soluble ($\text{Ca}(\text{OH})_2$ is sparingly soluble).</p>

It may be added that most chromates, oxalates, borates, and silicates, except those of the alkali metals, are insoluble in water. On the other hand, permanganates are usually soluble; and acid salts are in many cases more soluble than the normal salts.

487. **Alloys** — The word **alloy** is derived from the Lat. *alligare*, “to bind to.” Alloys are most commonly formed by melting together certain metals, such as copper and tin (bronze) or copper and zinc (brass). In primitive times alloys were produced by the simultaneous reduction of ores containing the constituent

metals. Thus, bronzes and the alloys of the precious metals were manufactured hundreds of years before the Christian Era; and brass was produced long before zinc was recognized as a distinct metal.

In some cases the metals combine to form compounds and in other cases solid solutions or mixtures are formed (Fig. 154). The composition of the former corresponds to the law of definite

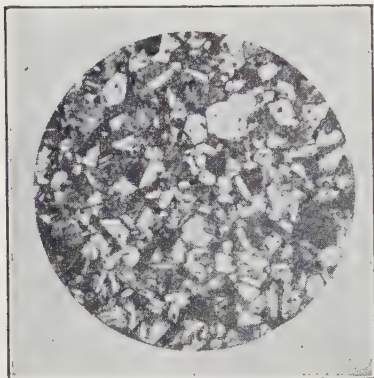


FIG. 154. Photomicrograph (D. P. Smith) of Ordinary Brass (Magnification 150) showing the somewhat confused crystalline structure. Shows particularly the "twinned crystals" characteristic of all alloys rich in copper, and of pure copper. This alloy is regarded as a *solid solution*.

proportions, while that of the latter does not. An ordinary brass shows only one kind of crystal ("mixed crystal"), both metals playing the same rôle in the crystal structure. When one of the metals is mercury, the alloy is called an **amalgam** (Greek, *a soft mass*). Thus, tin, zinc, gold, silver, sodium, etc., amalgamate quite readily when treated with mercury. Amalgams of iron, nickel, cobalt, manganese, and platinum cannot be easily prepared. They can be obtained, however, by the action of sodium amalgam on salts of these metals. The use of mercury in the extraction of gold and in gilding was made at an early date.

In recent years great progress has been made in the study of alloys, many of the results having been obtained by considering alloys to be solutions of the metals in each other. By means of the pyrometer such critical temperatures as the melting points have been determined, and the microscope has revealed the inner structure of the alloys. While a majority of alloys appear to be homogeneous to the eye, they are in fact heterogeneous. This may be shown by etching the polished surface of the metal alloy with a suitable reagent and then examining it under the microscope. The study of alloys is included in the science called Metallography.

The properties of an alloy are not the average of those of its components or constituents. To illustrate, an alloy containing 70 per cent of copper and 30 per cent of tin is white, while one

containing 70 per cent of copper and 30 per cent of zinc is pale yellow. Moreover, *the addition of a foreign metal lowers the melting point* (see Wood's metal, 643; also solder), *increases the hardness, and lowers the malleability as well as the conductivity for heat and electricity*. Thus, some of the copper tools employed by the ancients contained a low percentage of arsenic, which increased their hardness. Gold and silver are so soft that they are alloyed with other metals to increase their hardness. Copper wire containing only 0.03 per cent of arsenic has its conductivity for electricity lowered about 14 per cent.

Some metals (*e.g.*, tin and lead) can be mixed in all proportions. Others (*e.g.*, zinc and lead) are only miscible within certain limits. Thus, only 1.6 parts of zinc dissolve in 100 parts of lead.

While many of the properties of alloys follow the laws of solutions (Chap. IX), there are certain exceptions, which indicate, as stated before, the existence of definite compounds of the metals. Thus, the alloy AlSb has a melting point of $1,066^{\circ}$, while that of the metal aluminium is only 659° and antimony 630° . Copper and magnesium unite to form the compounds CuMg and Cu₂Mg.

Omitting the alloys of iron and steel, the chief metals used in the manufacture of alloys are as follows: Cu, Zn, Sn, Pb, Sb, Al, Ni, Mn, Mg, Cr, Bi, Cd, Ag, Au, Pt, and Hg.

The engineering importance of alloys could hardly be exaggerated. Practically nothing we use would be available without alloys, either entering into its composition or directly into its production.

Alloys as a class are noted for the facility with which they can be shaped — by casting, rolling, drawing, forging, welding, or machining — into forms in which their strength can be made use of. The alloys of iron are superior in strength and are relatively low in cost; but they are heavy and are subject to rusting. Where the weight is a disadvantage, aluminium and magnesium alloys are used; and where resistance to rusting is required, the copper alloys find use because of their permanence under conditions such that iron or steel would rust away.

488. Classification of the Metals. — With the object of further study, the metals may be divided into the following groups:

The Alkali Metals — Li, Na, K, Rb, Cs, (NH₄).

The Copper Group — Cu, Ag, Au.

The Alkaline Earth Metals — Ca, Sr, Ba, (Ra).¹

¹ The Radioactive Metals were treated in a previous chapter, because of their relation to the structure of matter (see Chap. IV).

The Magnesium Group — Be (Gl), Mg, Zn, Cd, Hg.

The Aluminium Group — Al and the Rare Earth Metals.

The Tin Group — Ge, Sn, Pb.

The Arsenic Group — As, Sb, Bi.

The Chromium Group — Cr, Mo, W, U.

Manganese.

The Iron Group — Fe, Co, Ni.

The Platinum Metals — Ru, Rh, Pd, Os, Ir, Pt.

EXERCISES

1. Is the division of elements into metals and non-metals satisfactory? State reasons for your answer.
2. State the physical characteristics of a metal. State three chemical properties of metals which differentiate them from non-metals.
3. What is the significance of the fact that certain metals lose electrons from their surfaces when exposed to ultra-violet light or when heated?
4. How may the conductivity of metals for electricity be explained?
5. Explain the action, if any, of water upon the following substances: PBr_5 , CuBr_2 , KBr , SbBr_3 , BaO , SeO_2 , and S_2O_7 .
6. Account for the fact that gold and platinum occur chiefly in the native state, while iron does not. Copper occurs in the free state and as sulfides, oxides, and basic carbonate. Can you offer any explanation as to why this is the case?
7. Define and also illustrate the following terms: mineral, ore, matrix (gangue), flux, and slag.
8. Define metallurgy. Through whose writings did the more important operations of metallurgy become known? Give a short biographical sketch of the author.
9. State some of the general principles involved in metallurgy. Name and also illustrate five methods for obtaining metals from their ores or compounds. What is aluminothermy?
10. Describe how you would concentrate a low-grade sulfide ore.
11. How would you obtain the metals from the following substances: SnO_2 , ZnS , Sb_2S_3 , AlCl_3 , Cr_2O_3 , CaCl_2 , NaOH , and $\text{Cu}(\text{OH})_2 \cdot 2\text{CuCO}_3$?
12. What is the difference between an electrolytic and an electrothermal process? Mention some important substances prepared by each process.
13. Define and illustrate alloy and amalgam. Are alloys compounds, ordinary mixtures, or solid solutions? State reasons for your answer. State the properties of alloys, and show how they differ from the pure metals.
14. Name some of the most important groups of alloys, giving their approximate composition and uses.
15. Place each of the following elements in its proper group or family: zinc, tin, potassium, aluminium, iron, antimony, copper, barium, lead, sodium, nickel, and gold; also arrange these metals in the order of their activity.
16. Outline several methods for preparing salts, and state the general rules governing the solubility of salts.

READINGS AND REFERENCES

- ARRHENIUS. Chemistry in Modern Life, Chap. IV.
DESCH. Metallography.
FOSTER. The Romance of Chemistry, Chaps. XVII and XVIII.
HOFMAN. General Metallurgy.
MEGRAW. The Flotation Process.
SLOSSON. Creative Chemistry, Chap. XIV.
WYSOR. Metallurgy.

CHAPTER XXVIII

THE ALKALI METALS

489. **Properties of the Metals of the Alkali Family.** — Some of the *physical properties* of these metals are given in the table below.

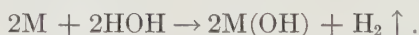
Element	Atomic Weight	Atomic Number	Density (Solid)	Melting Point	Boiling Point
Lithium, Li	6.94	3	0.534	186.0°	1400.0°
Sodium, Na	23.00	11	0.971	97.5°	877.5°
Potassium, K	39.10	19	0.862	62.3°	700.0°
Rubidium, Rb	85.45	37	1.532	38.5°	696.0°
Cesium, Cs	132.81	55	1.870	26.5°	670.0°

These are all very soft, malleable, and light metals, three of them being light enough to float upon water. When freshly cut, they are silvery white.

The chemical characteristics of the alkali metals are similar. They have a positive valence of one, an atom of each metal having a great tendency to lose an electron to form an ion:



They are the most basic and active of the metals, the activity increasing with increase in atomic weight. These metals quickly tarnish, therefore, when exposed to the air; and they all interact vigorously with cold water to form a base or alkali and free hydrogen:



With potassium, rubidium, and cesium the action is so violent, that the hydrogen ignites spontaneously. The hydroxides of these metals are the most active of the bases. These compounds can be subjected to very high temperatures without loss of water, while the hydroxides of other metals lose water more or less readily when heated, yielding the corresponding oxides. When the hydroxides or oxides of the alkali metals are dissolved in water or acids, much heat is evolved, which shows that these compounds

are strongly basic. Furthermore, their oxides cannot — with the exception of lithium oxide — be obtained by heating their carbonates or nitrates. As a rule, compounds of the alkali metals are readily soluble in water. Aqueous solutions of their normal salts of strong acids are generally neutral to indicators, showing that they are not appreciably hydrolyzed.

The alkali metals, when heated, unite with hydrogen to form hydrides, such as sodium hydride, NaH .

The hypothetical metal, **ammonium** (NH_4), has never been prepared, but it forms a series of compounds which are analogous to those of the alkali metals.

The compounds of potassium, rubidium, and cesium have very similar properties, but the physical properties of certain sodium and lithium compounds are quite different from those of the other three metals.

Lithium, the lightest of the group, is the least reactive of these metals, and in some respects resembles the metals of the alkaline earth group, as well as beryllium and magnesium.

In general, the alkali metals may be prepared by the electrolysis of the fused hydroxide or chloride, or by the interaction of the carbonate (except lithium) with carbon at a high temperature.

490. **Lithium, Li = 6.94.** — Lithium owes its name to a Greek word meaning *stony*, for at the time of its discovery it was believed that it occurred only in the mineral kingdom. Like rubidium and cesium, it is one of the rarer elements. In minute traces it is widely distributed; it occurs in quantity only in a few rare minerals, such as *petalite* and *lepidolite*. Its salts also occur in certain mineral springs and in the soil, being taken up by such plants as the beet and tobacco. Lithium compounds were recognized by Arfvedson in 1817, but the element was first isolated in quantity by Bunsen in 1858.

Lithium can be prepared by the electrolysis of its fused chloride; but it is better to employ a mixture of the bromide and chloride, because such a mixture has a lower melting point than has the pure chloride.

Lithium is the lightest solid known. The metal is softer than lead, but harder than the other metals of the alkali group. Its chemical properties are similar to those of sodium and potassium, but it is less active. The carbonate (Li_2CO_3) and the phosphate ($\text{Li}_3\text{PO}_4 \cdot 2\text{H}_2\text{O}$), unlike the corresponding compounds of the other alkali metals, are sparingly soluble in water. *Lithium compounds impart a bright-red color to the non-luminous flame, and the spectrum*

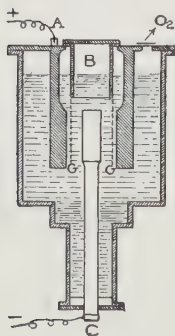
of lithium consists of a prominent crimson line and a feebler orange line.

"Lithia waters" are used for rheumatism, but they appear to be of doubtful value. Lithium salts are prescribed for gout and as a solvent for uric acid calculi or gravel, but their action in dissolving uric acid has been overrated. Owing to the introduction of organic drugs, the use of lithium salts in medicine has somewhat declined.

SODIUM. Na = 23

491. **Occurrence.** — Sodium occurs very abundantly as common salt (sodium chloride) in sea-water, in some inland lakes, and in beds which were deposited from solution. Sodium chloride constitutes more than two-thirds of the solid matter dissolved in sea-water. Sodium also occurs as the nitrate, or Chile saltpeter, NaNO_3 ; in many mineral silicates and in cryolite; in certain springs or inland lakes as the borate, carbonate, or sulfate. Rock-salt and sea-salt are usually the sources of other sodium compounds. Sodium constitutes about 2.5 per cent of the earth's crust, being one of the most abundant metals.

492. **Preparation.** — Sodium was first prepared by Humphry Davy, in 1807, by the electrolysis of moist sodium hydroxide. It is possible to imitate the Davy method by placing a short stick of moist sodium hydroxide in a silver or platinum dish and then joining the dish to the negative pole of a 100-volt direct current;



while a platinum wire joined to the positive wire of the main is brought in contact with the upper part of the stick of sodium hydroxide. The caustic soda melts and silvery globules of sodium appear on the dish, which constitutes the cathode. Owing to the cost of electricity and practical difficulties, the electrolytic method was not employed commercially until recent years.

Formerly, sodium was prepared by heating a mixture of sodium carbonate and carbon:

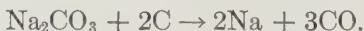


FIG. 155.

For many years sodium has been prepared on a commercial scale by the electrolysis of fused sodium hydroxide (Castner method). The caustic soda is melted in an iron vessel (Fig. 155) and the current passed through. The metal is liberated at the iron cathode (C) and rises and collects in a bell-

shaped vessel of iron (*B*). The wire gauze (*G*) permits the liquid to circulate, but prevents the circulation of globules of sodium. The sodium is removed from the bell by means of a perforated ladle. Hydrogen collects in the bell and escapes under the edges of the lid. Oxygen is liberated at the nickel-iron anode (*A*) and escapes through a hole in the lid of the iron cylinder. The optimum temperature for operation is about 300°. If the temperature is too high, the sodium interacts with sodium hydroxide, and is therefore lost:



493. **Properties.** — Sodium is a soft, malleable, silvery metal of density 0.971 and melting point 97.5°. The metal boils at 877.5°, giving a bluish vapor of density 12.75 ($H = 1$), which shows it is a monatomic gas. Sodium dissolves in liquefied ammonia, giving a blue solution. The metal tarnishes quickly in the air, and burns, when heated in air or oxygen, to form a mixture of oxides, including sodium peroxide, Na_2O_2 . It interacts with cold water to form hydrogen and sodium hydroxide, but not sufficient heat is generated to bring the escaping gas to its ignition temperature. Sodium forms an *amalgam*, which is an important reducing agent; it interacts with water to form hydrogen. Sodium amalgam is sometimes used instead of pure mercury in the extraction of silver and gold. The amalgam is less active than is sodium alone.

Sodium is used in the manufacture of sodium peroxide, sodium cyanide, sodium amalgam, and many organic compounds.

Sodium imparts a yellow color to the non-luminous flame, and its spectrum consists of a bright yellow line (really two lines very close together).

COMPOUNDS OF SODIUM

494. **Sodium Chloride, NaCl .** — Sodium chloride, or common salt, occurs very abundantly and widely distributed. Salt beds of enormous thickness are found, those at Sperenberg, Germany, reaching a thickness of 4,000 feet. The average thickness of the New York beds is 75 feet, and those of Michigan are, in certain localities, 400 feet thick. There are salt mines in Galicia said to be 500 miles long, 20 miles broad, and 1,200 feet thick. It has been estimated that the seas contain salt enough to cover the entire dry land to the depth of 400 feet; also, that the average person consumes directly or indirectly about 29 pounds of salt per annum in his food.

Salt is produced by mining, and by the evaporation of brine. Common salt usually contains magnesium chloride, which is very soluble and hygroscopic and therefore causes the salt to "cake" or become wet during humid weather. Starch or sodium bicarbonate is sometimes mixed with salt to prevent its caking. The former covers the particles and the latter interacts with the magnesium chloride to form the insoluble carbonate. Salt may be purified by recrystallization from water solution. "Chemically pure" sodium chloride is prepared by passing hydrogen chloride into a saturated solution of salt until the compound crystallizes out. The crystals are filtered by suction, washed with a little concentrated hydrochloric acid, and then dried.

Sodium chloride crystallizes in transparent cubes. The salt melts without decomposition at about 800° , and vaporizes at higher temperatures. Certain specimens of salt are blue, due, some believe, to colloiddally dispersed particles of metallic sodium.

Common salt is the source of other sodium compounds and of sodium and chlorine; it also is used extensively as a preservative and as an essential component of diet. Animals secure salt partially from grass and leaves; they sometimes travel long distances to find "salt-licks." Carnivorous animals secure necessary salts from the animals they eat.

100 g. of water at 0° C. dissolve about 35.7 g. of sodium chloride, and only slightly more at higher temperatures.

495. **Sodium Hydroxide, NaOH.** — *Sodium hydroxide*, or *caustic soda*, is one of the most important substances manufactured; it may be produced by several different methods:

(1) **By the interaction of water and sodium.** The product is very pure, but the method is employed for the production of only small quantities.

(2) **By the interaction of sodium carbonate and calcium hydroxide:**



The action is reversible, the best results being obtained when a 10 per cent solution of the carbonate is boiled with lime in an iron vessel. The calcium carbonate may be removed by filtration, and solid sodium hydroxide obtained by evaporation of the filtrate. This method is extensively employed.

(3) **By the electrolysis of sodium chloride.** The electric current is passed through brine, the products being sodium hydroxide, hydrogen, and chlorine. Various electrolytic cells have been

invented, one of the most successful being the Nelson cell (Figs. 156–157), which was adopted by the United States Government during the war, for the manufacture of chlorine at the Edgewood

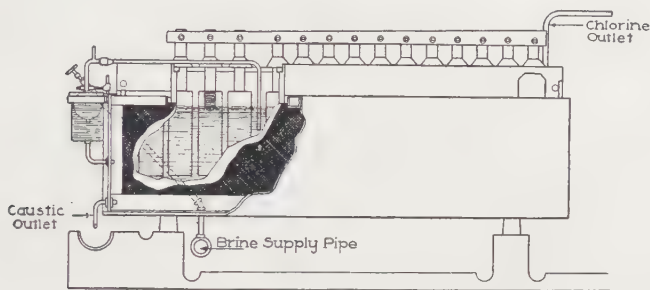


FIG. 156.

Arsenal, caustic soda and hydrogen being obtained as by-products and chlorine as the primary product.

There are serious difficulties to be overcome in all electrolytic processes for decomposing salt. The Nelson cell is of the diaphragm type, which means that the products of electrolysis are kept apart by employing a porous diaphragm in the cell. The body of the cell is a steel tank having an outlet for the solution of caustic soda. The anodes are constructed of graphite, and are separated from the cathode, a perforated steel plate, by means of a porous diaphragm of asbestos. A saturated solution of sodium chloride is maintained in the anode compartment at a constant level by means of the automatic brine feed. The chlorine gas, which is liberated at the anodes (due to the discharge of the chloride-ion), rises through the electrolyte and collects in the slate gas dome, whence it is discharged through a glass pipe. The electrolyte percolates through the asbestos diaphragm to the perforated steel cathode sheet, where hydrogen-ion is discharged leaving the hydroxide-ion along with the sodium-ion. In other words, a solution of caustic soda is obtained. This solution, which contains from 10 to 12

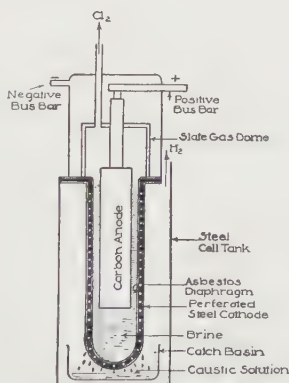


FIG. 157.

per cent of sodium hydroxide and rather more sodium chloride, is partially evaporated, whereupon salt separates, leaving the more soluble alkali in solution. By evaporating the caustic solution at a high temperature, sodium hydroxide is obtained, which may be cast into sticks. The plant at the Edgewood Arsenal had a capacity of 110 tons of caustic soda and 100 tons of chlorine every 24 hours. 3,552 Nelson electrolytic cells were installed in this plant.

Sodium hydroxide is also manufactured by the **Castner-Kellner method**. The Castner-Kellner cell is of a different type; it employs a moving mercury cathode, no diaphragm being used. The cell contains three compartments, and is given a slight rocking motion by means of a cam. The two outer compartments contain brine and graphite anodes. The central chamber contains sodium hydroxide and an iron cathode. A layer of mercury about one-eighth inch deep is placed upon the bottom of the cell. When the current is passed through, chlorine is liberated at the graphite anodes:



The sodium-ion is discharged upon the layer of mercury, and then dissolves in the latter to form an amalgam. The amalgam, due to a slight rocking motion of the cell, flows into the central compartment, where sodium hydroxide is formed and hydrogen discharged. By evaporation of the overflowing liquid, which contains about 20 per cent of alkali, solid caustic soda is obtained.

Sodium hydroxide is a white, brittle, deliquescent solid, which is extremely soluble in water; it is also soluble in ordinary alcohol. It may be purified by solution in alcohol, in which the carbonate is insoluble. Evaporation of the alcoholic solution yields the pure alkali. Sodium hydroxide is a powerful base and has, therefore, great affinity for carbon dioxide, forming the carbonate. Concentrated solutions of the hydroxide have a very corrosive action upon flesh, etc., hence its name caustic soda. The compound melts at 210° . Sodium hydroxide is used on a large scale in the manufacture of soap, for cleansing purposes (lye), in the petroleum industry, and in the manufacture of rayon, paper, and textiles. It is the cheapest of the very soluble, stable bases or alkalies.

496. Sodium Carbonate, Na_2CO_3 . — Sodium carbonate occurs in nature in large quantities. In Nevada and in California it is found as incrustations and in alkaline lake waters, due to deficient

rainfall and evaporation. The deposits of "natural soda" in our western states have been worked commercially in a number of places. There are also large foreign deposits of natural soda. Thus, in British East Africa there is a deposit which is estimated to contain at least 200,000,000 tons. Until the end of the eighteenth century, soda was obtained exclusively from the ash of seaweed, which meant more expensive soap and glass. This source of the carbonate no doubt explains the origin of the name "soda ash."

Sodium carbonate is manufactured on a very large scale from common salt. The compound is manufactured by two processes:

(I) The Leblanc Process, and (II) the Solvay (Ammonia) Process.

497. The Leblanc Process. — Toward the end of the eighteenth century Napoleon closed the European ports to English and American ships, which resulted in such a scarcity of sodium carbonate that a prize of 100,000 francs was offered for the invention of a profitable method for the production of the compound from sodium chloride. This prize was won by Nicolas Leblanc, an apothecary, in 1791, but he failed to receive his reward. As stated by Sir H. E. Roscoe: "It is sad that the man who thus originated a world-wide industry, and to whom we owe cheap soap and cheap glass, did not benefit from his discoveries, and, not receiving the reward promised by his government, died in 1806 by his own hand in poverty and despair."

The following is an outline of the method:

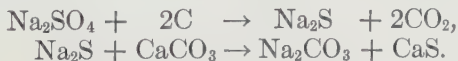
(1) Sodium sulfate (salt-cake) is produced by heating salt with sulfuric acid. The salt is first treated with sulfuric acid in a cast-iron or earthenware pan, sodium bisulfate, NaHSO_4 , being formed:



The bisulfate and the unchanged sodium chloride are raked out on the hearth of a reverberatory furnace (Fig. 158), and then heated to a higher temperature, which gives more hydrogen chloride together with *salt-cake* (Na_2SO_4):



(2) Sodium sulfate is heated with coal and limestone to form "*black ash*":



The black ash is now lixiviated, *i.e.*, treated with water, sodium carbonate going into solution, the calcium compounds being mostly insoluble. The solution contains various impurities and considerable sodium hydroxide.

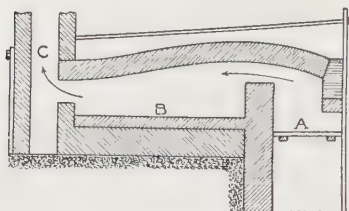


FIG. 158.

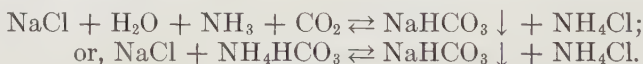
Sodium carbonate is prepared by carbonating, filtering, and evaporating the solution. The crystals are then dried completely by heat, and the product, "soda ash," contains 98–99 per cent of Na_2CO_3 . By dissolving soda ash

in water and allowing the solution to crystallize below 32° , sal soda or washing soda, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, is obtained.

In the manufacture of soda by the Leblanc process, hydrochloric acid is obtained as a by-product. Owing to the discovery of a better method for the production of soda, the Leblanc process has been declining. It is still used to some extent in England, but the black ash liquor is usually converted directly into sodium hydroxide by treatment with lime.

498. The Solvay (Ammonia) Process. — This process is the leading one for the manufacture of soda. The reactions upon which the process is based were known as early as 1852, but the mechanical details for the commercial production of the compound were not perfected until the latter part of the sixties. This we owe to the Belgian chemists, Ernest and Alfred Solvay.

Brine is saturated with ammonia and then treated with carbon dioxide, in consequence of which sodium bicarbonate separates out:



The reactions are really ionic, the bicarbonate-ion (from NH_4HCO_3) combining with the sodium-ion to form sodium bicarbonate:



The bicarbonate is sparingly soluble in a solution containing ammonium chloride and ammonium bicarbonate.

Ammoniacal brine is delivered to a "carbonating tower," which is divided by a number of perforated partitions (Fig. 159). The carbon dioxide enters under the lowest dome, and rises in small bubbles through the perforations. A thick, milky liquid,

containing NaHCO_3 in suspension and NH_4Cl and NaCl in solution, is drawn off at the bottom, the bicarbonate removed by filtration, and the filtrate is then treated with lime to recover ammonia, calcium chloride being obtained in large amount as a by-product.

The bicarbonate is calcined to obtain soda ash and carbon dioxide, and the latter is again used to produce more bicarbonate:



The chief advantages of the Solvay process are: (1) it yields a purer product than the Leblanc process; (2) the cost of manu-

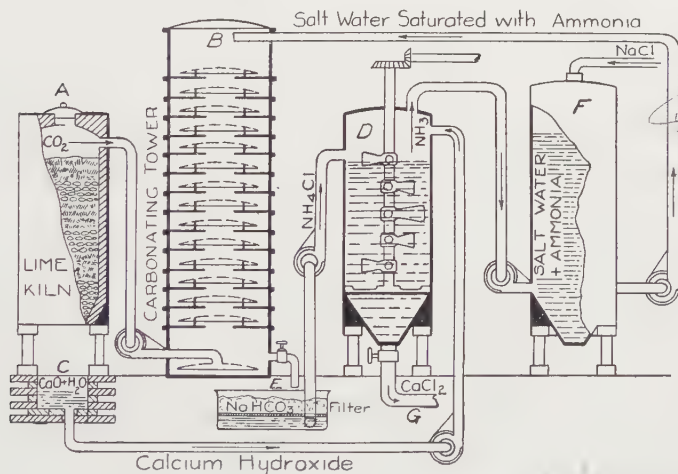


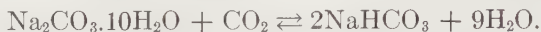
FIG. 159.

facture is lower; and (3) no noxious by-products are formed. The ammonia soda ash contains from 99 to 99.7 per cent of Na_2CO_3 .

Sodium carbonate is very soluble in water, and its aqueous solution has a strongly alkaline reaction (explain). The decahydrate, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, is commonly known as "washing soda" or "sal soda"; it consists of large monoclinic crystals. Sodium carbonate is used on a large scale for the manufacture of glass, caustic soda, soap, sodium bicarbonate, paper and pulp, and in the softening of water, etc.

499. Sodium Bicarbonate, NaHCO_3 . — Sodium bicarbonate, sodium hydrogen carbonate, or baking soda, is prepared by the

Solvay process, or by treating the decahydrate with carbon dioxide:

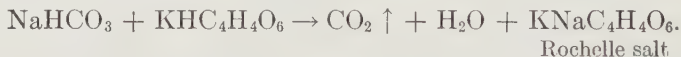


Refined sodium bicarbonate is produced by dissolving soda ash in water, carbonating the solution, filtering off the sodium bicarbonate, centrifuging, and then drying.

Sodium bicarbonate is soluble in water and the solution of the pure salt is distinctly alkaline to methyl orange, but only slightly alkaline to phenolphthalein at room temperature. It owes its alkalinity to slight hydrolysis. Sodium bicarbonate is used extensively for the manufacture of baking powders, for baking with sour milk, for neutralizing acids, and in medicine.

500. Baking Powders. — In baking, carbon dioxide is liberated from sodium bicarbonate, which passes through the bread and aerates it, or causes it to rise. The dioxide is set free by treating the bicarbonate with sour milk, or by mixing it with an acidic substance, such as cream of tartar or an acid phosphate. When the baking powder is treated with water, the gas is evolved.

Cream of tartar baking powders contain sodium bicarbonate, cream of tartar (potassium bitartrate, $\text{KHC}_4\text{H}_4\text{O}_6$), and starch or flour (to prevent the interaction of the components). On the addition of water, the following change occurs:



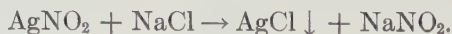
The primary phosphates, NaH_2PO_4 and $\text{Ca}(\text{H}_2\text{PO}_4)_2$, may be substituted for cream of tartar.

501. Other Sodium Compounds. — **Sodium nitrate**, NaNO_3 , occurs abundantly in South America, and is commonly called Chile saltpeter. It is the most abundant of the natural nitrates, is very soluble in water, from which it crystallizes in rhombohedra. When heated, it yields sodium nitrite and oxygen:



Sodium nitrate is used in immense quantities as a fertilizer and for the manufacture of nitric acid (387).

Sodium nitrite, NaNO_2 , is prepared by heating sodium nitrate with lead, a reducing agent. The salt may be obtained in a purer state by treating a solution of silver nitrite with sodium chloride:



When the filtrate from the precipitate of silver chloride is evaporated, white, deliquescent crystals are obtained. The salt is used for the manufacture of coal-tar dyes and as a chemical reagent.

Sodium sulfate, Na_2SO_4 , may be obtained by treating sodium hydroxide with sulfuric acid or by the interaction of sodium chloride and sulfuric acid (292). If an aqueous solution of the salt is allowed to crystallize below 32.4° , Glauber's salt, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, is formed; but if the solution is evaporated above 32.4° , the anhydrous salt, Na_2SO_4 , separates out (175).

Sodium sulfate is used in the manufacture of glass, paper pulp, and sodium sulfide. It is also used in dyeing and tanning and in medicine, its physiological action being somewhat similar to that of Epsom salts. The salt is contained in certain mineral waters, such as those of Karlsbad.

Sodium cyanide, NaCN , may be prepared by heating calcium cyanamide with salt and carbon:



Sodium cyanide is highly soluble in water and the solution is strongly alkaline (why?) and very poisonous. It is used extensively as a solvent for silver and gold (see Cyanide Process), in electroplating, and as a source of hydrocyanic acid for fumigation.

Sodium silicates, such as Na_2SiO_3 and Na_4SiO_4 , are formed by fusing silica with caustic soda or sodium carbonate, or by boiling silica in a digester with a solution of sodium hydroxide (456). The composition of ordinary "water glass" may vary from $\text{Na}_2\text{SiO}_3 \cdot \text{SiO}_2$ to $\text{Na}_2\text{SiO}_3 \cdot 3\text{SiO}_2$. It is used for the manufacture of laundry soap; as an adhesive; as a binder in abrasive wheels, and in acid-proof and heat-resisting cements; in preserving eggs, silk weighting, etc.

Sodium tetraborate or **borax**, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, occurs as a mineral and is also manufactured. When the borax is crystallized below 60° , the decahydrate is obtained; but at higher temperatures the pentahydrate is formed. A solution of borax is strongly alkaline, due to hydrolysis. The salt has many uses (467).

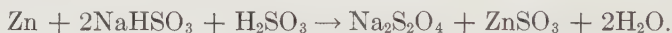
Sodium phosphate, $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$, is manufactured from phosphate rock. Phosphoric is obtained by treating the rock with sulfuric acid; soda ash is then added, and the solution allowed to crystallize. The salt is used in the textile industry, in the manufacture of baking powder, as a softener of water, and in medicine.

Sodium peroxide, Na_2O_2 , is prepared by burning metallic sodium in excess of air or oxygen. The oxide thus prepared is mixed with the lower oxide, Na_2O . The compound is used in chemical analysis as an oxidizing agent, in bleaching, for generating oxygen in hospitals, in submarines, and in mine-rescue apparatus, and as a source of hydrogen peroxide.

Sodium perborate, $\text{Na}_2\text{B}_4\text{O}_8 \cdot 10\text{H}_2\text{O}$ or $\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$ (according to method of manufacture) is prepared by suspending borax in a solution of sodium carbonate which is being electrolyzed. It is used in the laundry, in bleaching cotton and linen, and for hygienic purposes. It injures fabrics less than do many more active oxidizing agents. The salt is an oxidizing agent, its solution yielding H_2O_2 when treated with sulfuric acid, or by merely heating.

Sodium sulfide, Na_2S , may be prepared by heating salt-cake, Na_2SO_4 , with coal. It is more economically manufactured, however, from niter-cake (NaHSO_4), sodium chloride, and coal. The salt is very soluble in water and the solution is strongly alkaline. It is used in dyeing, for removing hair from skins, in the manufacture of dyes, in sulfurizing lead and copper ores preparatory to flotation, etc.

Sodium hyposulfite, $\text{Na}_2\text{S}_2\text{O}_4$, is used by the calico printer and dyer as a reducing agent for indigo. A solution of the salt may be obtained by the interaction of zinc, sodium bisulfite, and sulfurous acid:



Sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, is commonly called "sodium hyposulfite," or simply "hypo." It is prepared by treating a solution of sodium sulfite with sulfur; also by boiling sulfur with caustic soda solution:



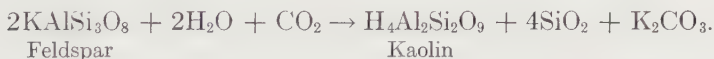
By crystallization of the solution, large, monoclinic crystals of the pentahydrate are obtained. It is used in the leather trade, in the textile industry for removing the last traces of chlorine from bleached fabrics, in bleaching (source of SO_2) and in dyeing, and in photography as a fixing agent (solvent for silver salts), etc. The salt is decomposed by acids:



502. **Analytical.** — Virtually all sodium compounds are soluble in water. Sodium fluosilicate, Na_2SiF_6 , and sodium hydrogen pyroantimonate, $\text{Na}_2\text{H}_2\text{Sb}_2\text{O}_7$, are the least soluble, being the only ones obtainable by precipitation. The sodium-ion, Na^+ , is colorless. The gas flame is colored yellow by all sodium compounds. Since the flame test is a very delicate one and sodium compounds are widely distributed, great care has to be exercised in testing for sodium.

POTASSIUM. K = 39.1

503. **Occurrence.** — Potassium compounds are widely distributed in nature, being found in rocks, all fertile soils, the ocean, saline residues, inland waters, and in plants and animals. The earth's crust contains nearly 2.5 per cent of potassium. The element is an essential constituent of many minerals: *e.g.*, feldspar and mica. Silicate rocks containing potash occur in enormous deposits. By the weathering of the rocks, potash finds its way into the soil, as well as into the rivers, lakes, and ocean. The most abundant minerals occurring in igneous rocks are the feldspars. Potash feldspar is called orthoclase (KAlSi_3O_8), and soda feldspar, albite ($\text{NaAlSi}_3\text{O}_8$). By the weathering of potash feldspar, kaolin or clay, silica or quartz, and potassium carbonate are formed:



This change explains, in part, the formation of soil together with the potash contained therein, as well as the formation of clay, which is so abundant and widely distributed.

Salt deposits, as a rule, contain potash, but generally in very small quantity. The chief known deposits are in Germany (Stassfurt), Alsace, Poland, California (Searles Lake), and in the western part of Texas.

It is estimated that the potash in reserve in tons of K_2O is as follows:

Germany.....	2,000,000,000
Alsace.....	300,000,000
Searles Lake, Calif.....	20,000,000

Potash occurs at Stassfurt in the upper layers of rock salt, in the plains of northern Germany. It is estimated that Ger-

many has sufficient potash to supply the world for 2,000 years at the present rate of consumption. Potash is found in salt beds as *sylvite*, KCl ; *carnallite*, $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$; *schoenite*, $\text{MgSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$; and *kainite*, $\text{MgSO}_4 \cdot \text{MgCl}_2 \cdot \text{K}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$.

Poland has one of the largest deposits of potassium salts in Europe, the production in 1926 being 210,000 tons.

Potash also may be obtained as a by-product of the blast furnace and of the manufacture of cement, from the kelp of the Pacific coast, and from molasses waste, wood ashes, wood washings, etc.

The "potash problem" was a very vital one in connection with the Great War, for the supply from Germany was cut off in 1915. After 1915, the rest of the world, outside of the Central Powers, was forced to produce as much potash as possible. In 1918 the United States produced about 55,000 tons, calculated as K_2O , from 10 distinct classes of raw materials. About 73 per cent was produced from natural brines and 9 per cent from kelp. After the signing of the Armistice in November, 1918, a crisis came in the American potash industry, and by the early part of 1919 nearly all producers had shut down and some had closed out their business.

Before the war, the annual importation of potash (calculated at K_2O) from Germany was about 240,000 tons.

504. Preparation and Properties. — Potassium was first prepared by Davy, in 1807, by the electrolysis of fused potassium hydroxide. He placed some caustic potash in a silver dish, heated it to fusion, and then passed an electric current through the molten mass, the dish serving as cathode. Much to his surprise, he observed the formation of silvery globules, which ignited spontaneously. Davy was so excited that "he began to dance and it was some time before he could control himself to continue his experiments." The methods used for the preparation of the metal are the same as those used for sodium. As the metal has no particular use, very little of it is produced.

Potassium is a soft metal, possessing a silvery luster. Its chemical properties are similar to those of sodium, but it is more active. Thus, when potassium is brought in contact with cold water, so much heat is generated that the liberated hydrogen ignites, and burns with a violet flame, due to the vapor of the metal.

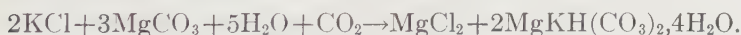
POTASSIUM COMPOUNDS

In general, the compounds of potassium are similar to those of sodium, but in a few cases the salts of potassium are decidedly less soluble than the corresponding sodium salts.

505. **Potassium Hydroxide, KOH.** — Caustic potash is manufactured by the methods used in the production of sodium hydroxide. The two compounds have similar properties, but for commercial purposes the cheaper sodium compound is generally used. It is utilized in the manufacture of soft and liquid soaps and for absorbing carbon dioxide. Potassium oxide (K_2O) can be obtained by the action of potassium on the hydroxide.

506. **Potassium Chloride, KCl.** — This salt occurs in large quantities in nature, especially in the salt deposits of Stassfurt and of Alsace. **Sylvite** is nearly pure potassium chloride, and **carnallite** is a double chloride, $KCl \cdot MgCl_2 \cdot 6H_2O$. Potassium chloride is also produced from kelp, brine, etc. The properties of the salt are very similar to those of sodium chloride. It is used very extensively as a fertilizer and as the source of other potassium compounds.

507. **Potassium Carbonate, K_2CO_3 .** — This salt may be prepared from potassium chloride by the Leblanc process; it may also be obtained from wood ashes and wool fat. On the commercial scale, however, it is usually prepared from potassium chloride and magnesium carbonate. The chloride, water, magnesite ($MgCO_3$) and carbon dioxide are heated under pressure:



When the double salt of magnesium and potassium is heated with water to 120° , a solution of the carbonate is obtained:



Potassium carbonate is used largely in the manufacture of hard glass, soft soap, potassium hydroxide and other potassium compounds, in wool washing, and in bleach and dye works. Its properties are similar to those of sodium carbonate. In commerce the salt is often called *pearl ash*.

Potassium bicarbonate, $KHCO_3$, is also similar to the corresponding sodium salt. Formerly, the salt was called *saleratus* (Lat., *aerated salt*), a name now sometimes applied to baking soda.

508. **Potassium Nitrate, KNO_3 .** — This salt is commonly termed **saltpeter** or **niter**. It occurs in the surface soils in the vicinity of certain Oriental villages and cities. Potassium nitrate is manufactured by boiling together concentrated solutions of Chile saltpeter ($NaNO_3$) and potassium chloride. These salts interact by double decomposition and the less soluble sodium

chloride separates from the hot solution; it is removed by filtration, and potassium nitrate is obtained by cooling the filtrate (175). Potassium nitrate is extremely soluble in water at 100°, but only moderately soluble at 10°. The solubilities at 10° and 100° of the four salts involved are given below.

GRAMS OF SALT SOLUBLE IN 100 GRAMS OF WATER

	At 10°	At 100°
KNO ₃	21	246
NaCl.....	36	40
KCl.....	31	56
NaNO ₃	81	180

The manufacture of potassium nitrate from Chile saltpeter was introduced during the Crimean War (1852–1855), on account of the insufficient supply.

Potassium nitrate yields oxygen, when heated, and is therefore a good oxidizing agent. Its chief uses are in the manufacture of black powder and pyrotechnics, as an oxidizing agent, a preservative for meats, a fertilizer, and in medicine. **Black powder** is a mixture of potassium nitrate, sulfur, and charcoal (carbon); it is used in blasting, in blank-fire charges, in base charges for shrapnel shells, in primers and fuses, in mixtures for small-arms ammunition, and as a detonator. Sodium nitrate is too hygroscopic to be used for these purposes. When gunpowder explodes, immense volumes of gases at a temperature over 2,000° are generated. In 1914, nearly 30,000,000 pounds of potassium nitrate were produced in the United States.

509. Other Potassium Compounds. — Potassium chlorate, KClO₃, is produced by electrolyzing a concentrated solution of potassium chloride. In case the products of electrolysis are kept apart by a diaphragm (495), chlorine and potassium hydroxide are obtained; but in the absence of a diaphragm and by keeping the liquid cool, potassium hypochlorite is formed:



In a hot solution, however, the hypochlorite yields the chlorate:



Potassium chlorate, like potassium nitrate, crystallizes more readily from water solution than does the corresponding sodium

compound. It is an active oxidizing agent, and is used in matches, pyrotechnics, magnesium flash-light powders, detonators, percussion caps, medicine, preparing oxygen, etc.

Potassium permanganate, KMnO_4 , is a good oxidizing agent and disinfectant. It may be obtained by treating a solution of potassium manganate (K_2MnO_4) with chlorine, ozone, carbon dioxide, or an acid; or by effecting the oxidation of the manganate by means of the electric current. The salt is obtained as purple crystals, which are readily soluble in water. Potassium permanganate is also used in bleaching, in dyeing shoe leather, for coloring wood a deep brown, and as an oxidizing agent. A dilute aqueous solution of potassium permanganate is used for allaying the irritation and itching produced by the poison ivy.

Potassium sulfate, K_2SO_4 , is manufactured from kainite ($\text{MgSO}_4 \cdot \text{MgCl}_2 \cdot \text{K}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$) and by treating potassium chloride with sulfuric acid. It is used as a fertilizer, in the preparation of alum and potassium carbonate, and in medicine.

Potassium chromate, K_2CrO_4 , is produced by treating a solution of potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) with potassium carbonate or hydroxide. The salt is obtained by evaporation, in the form of beautiful yellow crystals; it is used in tanning.

Potassium bromide, KBr , is used extensively in pharmacy, in photography, and as a chemical reagent; it is a valuable medicine, especially for nervous disorders.

Potassium iodide, KI , is used extensively in medicine, particularly in the treatment of scrofulous and syphilitic diseases; it is also used in photography.

Potassium cyanide, KCN , has been largely replaced by the cheaper sodium cyanide (501). It still finds application in electroplating, in photography, and as an insecticide, etc.

Potassium sulfide, K_2S , finds extensive use in photography, in toning prints, and in dyeing.

Potassium bitartrate, $\text{KHC}_4\text{H}_4\text{O}_6$, is the principal component of wine lees (solid matter collected from the bottom of wine casks) and argol (crystalline deposit on the sides of the casks), and cream of tartar. Cream of tartar is prepared from argol by recrystallization, and it is used in preparing baking powders, in candy, and in the manufacture of tartaric acid and tartrates.

510. Analytical. — Nearly all potassium compounds are soluble in water. Potassium may be precipitated, however, as potassium bitartrate, $\text{KHC}_4\text{H}_4\text{O}_6$, and as potassium chloroplatinate, K_2PtCl_6 (yellow crystals). The latter compound is much less soluble in

alcohol. Other sparingly soluble salts are the perchlorate (KClO_4) and the fluosilicate (K_2SiF_6). The potassium-ion, K^+ , is colorless. Potassium imparts a violet color to the non-luminous flame, and its spectrum exhibits a prominent red line and one in the violet.

511. The Spectroscope. — When a narrow beam of white light is permitted to pass through a transparent prism (*e.g.*, of glass), the white light suffers dispersion, *i.e.*, it is broken up into the colors of the rainbow. In other words, a *spectrum* is produced, which may be received upon a screen (Fig. 160). In passing through the prism, the red rays (longest wave-

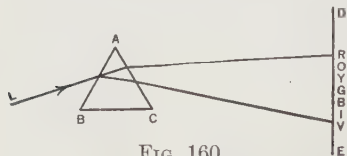


FIG. 160.

length) are refracted to the least extent, and the violet rays are the most refracted. A beam of white light gives a continuous spectrum, the series of color running from red through orange, yellow, green, blue, indigo, to violet.

About 1860 an instrument known as the spectroscope was invented by Bunsen and Kirchhoff, and it has been a powerful instrument in scientific research.

The ordinary spectroscope (Fig. 161) consists of (1) a triangular prism, which disperses the light rays of different wave-lengths; (2) a tube (*A*) provided with a narrow slit, which admits the light; and (3) a small telescope (*B*), through which the spectrum is viewed; and (4) a scale (*C*) for determining the relative positions of the lines. Now, when the light comes through the slit from the vapor of sodium heated in the non-luminous flame of a burner, a brilliant yellow line is visible (really two yellow lines lying very close together). No other substance gives these lines. Potassium gives two lines — one red and the other deep blue; helium gives many lines, one of which — the orange line — in particular was observed in the solar spectrum in 1868. Each element under suitable conditions exhibits a characteristic spectrum (Fig. 162).

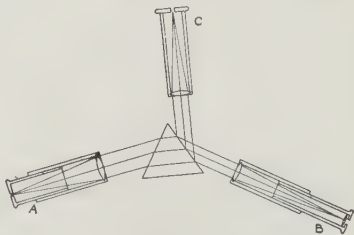
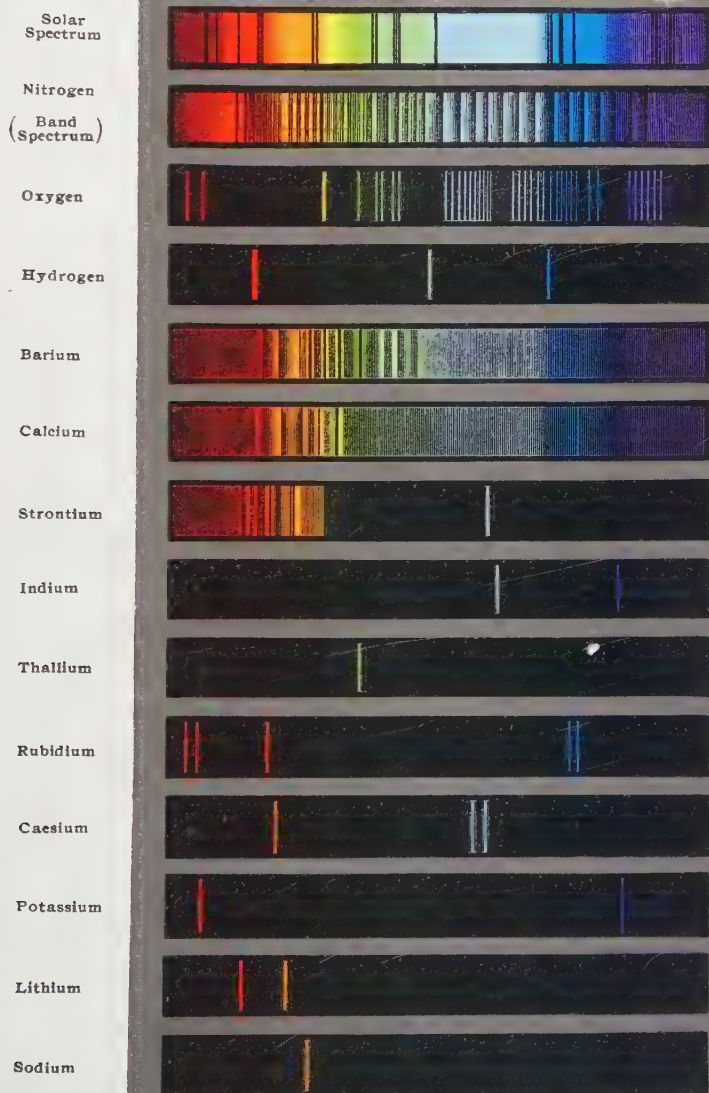


FIG. 161.

The principles upon which spectrum analysis is based were announced by Kirchhoff in 1858. They may be stated thus:

Emmissions-Spectra.



(1) A continuous spectrum is given by every incandescent body, the molecules of which so interfere with each other as to prevent their free, independent, luminous vibration; that is, by solid or liquid bodies, or by gaseous bodies under high pressure.

(2) The spectrum of an element in the gaseous state, under low pressure, is discontinuous, made up of bright, characteristic lines.

(3) A gaseous substance absorbs from white light passing through it precisely those rays of which its own spectrum consists. Under such conditions the spectrum is reversed, *i.e.*, black lines appear instead of bright ones. The solar spectrum, *e.g.*, is crossed by a great number of dark lines which are due to the presence of gases in the envelope surrounding the incandescent center of the sun. These dark lines are termed the **Fraunhofer lines**. The spectrum in which they appear is known as an absorption spectrum.

By sealing a gas in a highly evacuated tube provided with electrodes (Plücker tube) and applying a high voltage to the electrodes, the rarefied gas becomes brilliantly luminous (Fig. 163). When the light in the narrow part of the tube is examined with

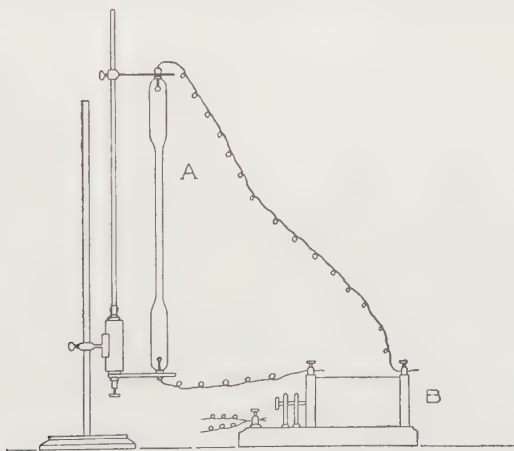


FIG. 163. Plücker Tube.

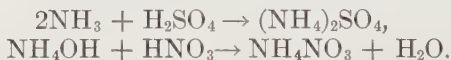
a spectroscope, a characteristic spectrum is found for each gas (*vacuum-tube spectrum*).

512. **Rubidium and Cesium.** — Soon after the invention of the spectroscope, Bunsen announced, in 1860, the discovery of cesium, a new alkali metal; and in 1861 he also discovered by means of spectrum analysis a second alkali metal, which he named rubidium. Bunsen discovered these metals in the waters of Durkheim and in the mineral petalite. They are rare elements, and are very similar to potassium in most respects, but are more electropositive.

In general, their salts are similar to those of the other alkali metals, particularly potassium. The element *cesium* (Lat., *caesius*, bluish-gray) owes its name to the fact that it gives blue lines in its spectrum, and *rubidium* (Lat., *rubidus*, red) owes its name to the red lines.

513. Ammonium Compounds.—The name **ammonium** is applied to the metallic radical, NH_4 , which has never been obtained in the free state. It is probable, however, that a solution of ammonium in mercury (ammonium amalgam) can be obtained by the electrolysis of an ammonium salt (e.g., NH_4Cl) with a pool of mercury as cathode, or by placing sodium amalgam in a strong solution of the salt.

Ammonium compounds are similar, in some respects, to the corresponding compounds of the alkali metals. This is especially true as regards solubility and crystalline form. Ammonium salts are very closely related to those of rubidium. Ammonium salts are easily prepared by treating ammonia or ammonium hydroxide with acids:



All ammonium compounds are decomposed by heat. When a mixture containing salts (e.g., the chlorides) of ammonium, sodium, and potassium is ignited, the ammonium salt is volatilized leaving the sodium and potassium compounds behind. Nearly all ammonium salts are soluble in water.

Ammonium sulfate, $(\text{NH}_4)_2\text{SO}_4$, is obtained in immense quantities as a by-product of the coke-oven and gas works. It is a white, crystalline salt, and is chiefly used as a fertilizer.

Ammonium nitrate, NH_4NO_3 , is used as a source of nitrous oxide, and in the manufacture of explosives and fireworks. During the recent war large amounts of the salt were used as a high explosive. When the compound is detonated, it explodes violently. *Amatol*, a mixture of ammonium nitrate and trinitrotoluene (TNT) was used by the Allies for filling high explosive shells. *Ammonal*, which was extensively used as an explosive, consists of ammonium nitrate and powdered aluminium (and sometimes charcoal and potassium nitrate).

Ammonium chloride or **sal ammoniac**, NH_4Cl , is used in soldering, in the preparation of ammonia, in the manufacture of dry cells, in medicine, and as a chemical reagent. It may be readily purified by sublimation.

Ammonium carbonate, $(\text{NH}_4)_2\text{CO}_3$, is unstable; it decomposes at ordinary temperatures, yielding ammonia and the bicarbonate $(\text{NH}_4\text{HCO}_3)$, which is much more stable:



Ammonium sulfide, $(\text{NH}_4)_2\text{S}$, may be formed in solution by treating ammonia water with hydrogen sulfide:



The compound is almost completely hydrolyzed by water into the acid sulfide (NH_4HS) and ammonium hydroxide. The acid sulfide may be formed in solution by treating ammonia water with an excess of hydrogen sulfide:



The ammonium sulfides are unstable, and are used in chemical analysis.

The ammonium-ion (NH_4^+) is colorless and, like the potassium-ion, yields a sparingly soluble bitartrate $(\text{NH}_4\text{HC}_4\text{H}_4\text{O}_6)$ and chloroplatinate $((\text{NH}_4)_2\text{PtCl}_6)$. When an ammonium salt is warmed with a solution of an alkali, ammonia is evolved (376).

EXERCISES

1. Name the metals of the alkali family, giving symbols, and tabulate their physical and chemical properties. Show that their natural modes of occurrence suggest that they are analogous.
2. Prepare a tabular summary of the characteristic chemical properties of the compounds of the alkali metals, including the oxides, hydroxides, hydrides, and chief salts.
3. Outline the general methods which may be employed in preparing the alkali metals. Describe in detail the Castner process for sodium.
4. The lowest temperatures at which the alkali metals interact with water are as follows: Na — 98° , K — 105° , Rb — 108° , Cs — 116° . What are the relative degrees of the electropositiveness of these metals? Can you cite other properties which have a bearing on the electropositiveness of the alkali metals?
5. Show by chemical equations that the alkali metals are good reducing agents.
6. Outline the occurrence, preparation, purification, properties, and uses of sodium chloride. Explain the fact that some specimens of rock salt are blue. Why does salt decrepitate when heated?
7. Outline two commercial methods for the manufacture of sodium hydroxide, and name any by-products obtained. What are its properties and uses? How would you transform NaOH into Na_2O ?

8. How may sodium sulfate be reduced to sodium sulfide? How could sodium nitrate be produced from sodium sulfate?

(9) Write the ~~ionic~~ equations involved in the manufacture of soda by the Solvay process. What advantages has the Solvay process over the Leblanc process?

(10) When fresh crystals of washing soda are examined, they are coated with a white powder. Explain. How may sodium bicarbonate be prepared from washing soda?

11. Explain the action (if any) of water upon sodium carbonate and upon sodium bicarbonate.

12. Give the composition of a good baking powder. Write chemical equation to show what occurs when the powder is employed in baking.

13. Write the formulae for all the sodium salts of orthophosphoric acid, and explain what occurs when each of the salts is dissolved in water. How may these salts be prepared?

14. State the chief sources of potash, and explain the weathering of feldspars.

15. Outline fully the transformation of Chile saltpeter into potassium nitrate. How may potassium nitrite be formed from potassium nitrate?

16. Write chemical equations for the preparation of KClO , KClO_3 , and K_2PtCl_6 .

17. Outline the principles of the spectroscope and of spectrum analysis. How may the spectrum of a gas, such as helium or hydrogen, be obtained?

18. State the general characteristics of ammonium compounds. What is their chief source? Compare and contrast them with corresponding compounds of sodium and of potassium.

19. How would you prepare a solution of ammonium sulfide? Why does the solution smell of ammonia and of hydrogen sulfide?

20. How may sodium, potassium, and ammonium (say, as the chlorides) be separated and identified?

21. What evidence have we to show that sodium vapor is a monatomic gas?

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CHAPTER XXIX

THE COPPER GROUP

514. General Characteristics and Relationships. —

Element		Atomic Weight	Atomic Number	Density	Melting Point	Boiling Point
Copper,	Cu	63.57	29	8.93	1083°	2300°
Silver,	Ag	107.88	47	10.49	960.5°	1950°
Gold,	Au	197.2	79	19.32	1063°	2600°

Copper, silver, and gold fall in Group I of the Periodic System and are known as the *coinage metals* because they are universally used in coinage. They are related in a way to the alkali metals, which are members of Sub-group I A, while the coinage metals belong to Sub-group I B. The chemical relationship of these two sub-groups is not close, but all the elements are univalent. Copper is also bivalent and gold trivalent. The oxides and hydroxides of the alkali metals are strongly basic, while those of the Copper Group (except Ag_2O) are feebly so. The alkali metals are exceedingly active; while the other metals are among the most inactive of the metals, all being found native and only copper being oxidized in the air. The alkali metals never enter into anions or complex ions, while copper, silver, and gold do: *e.g.*, K.Cu(CN)_2 , K.Ag(CN)_2 , K.Au(CN)_2 . The halides of the alkalies are soluble in water and are not hydrolyzed by it; the halides of silver, univalent copper (Cu_2Cl_2), and gold (AuCl) are virtually insoluble; and the halides of copper and of gold are partially hydrolyzed by water. Furthermore, the affinity for oxygen diminishes as the atomic weight increases from copper to gold; and compounds of gold and of silver are more reducible than are compounds of copper. Thus, ferrous sulfate readily precipitates gold from solutions of its salts, silver less readily, but not copper. These metals are easily deposited quantitatively from solution by electrolysis.

It also is interesting to note that the metals of the Copper Group are related on the one hand to zinc, cadmium, and mercury

(Sub-group II B) and on the other to nickel, palladium, and platinum. This relationship is shown below:

Ni (58.69)	Cu (63.57)	Zn (65.4)
Pd (106.7)	Ag (107.88)	Cd (112.4)
Pt (195.2)	Au (197.2)	Hg (200.6)

This is an illustration of the general rule that “*the properties of an element are the mean of those of its atomic analogues, that is, of adjacent elements in series and in group.*” An examination of the Periodic Table shows that palladium, cadmium, copper, and gold are the atomic analogues of silver.

The metals of the copper group are malleable and ductile and are excellent conductors of heat and electricity.

Gold and silver and the metals of the Platinum Group are called the “noble metals,” the “noble” character of the element in the group increasing with increasing atomic weight. Being quite inactive, the metals of the Copper Group occur in the free state, and have but little tendency to form ions. Copper, silver, and gold were all known to the ancients, who represented copper by the symbol ♀, the looking-glass of Venus; silver by ☾, *luna* (the moon); and gold by ☼, *sol* (the sun).

COPPER. Cu = 63.57

515. **Occurrence.** — **Copper** (Lat. *cuprum*, from earlier *Cyprium*, *Cyprium aes*, i.e., Cyprian brass, from Greek *Cyprus*, anciently renowned for its copper mines) was perhaps the first metal employed by man, due to the fact that it occurs in quantity in the free state. The “copper age” followed the “stone age.”

In the native state copper occurs in large masses in the Lake Superior district, where it has been produced on a commercial scale since 1845. To the end of the year 1918 Michigan had produced over 6,500,000,000 pounds of copper, or about 24 per cent of the output from the United States since 1845; and the Lake Superior region is unique in that it is the only district in which a large output is derived from native copper. The native metal almost always contains small quantities of silver and a few other metals. One mass of 400 tons of native copper was found in a Minnesota mine. The Indians worked the copper of the Lake Superior district long before the arrival of the white man.

Copper occurs in small quantity in most igneous rocks. It also is found in combination in some plants and animals: for

instance, in the feathers of certain birds and in the blood of the cuttlefish.

In addition to native copper, the *chief copper ores* are as follows:

Chalcopyrite (copper pyrites)	CuFeS_2 (generally present in copper mines)
Chalcocite	Cu_2S
Bornite	Cu_3FeS_3
Malachite	$\text{Cu}(\text{OH})_2 \cdot \text{CuCO}_3$
Azurite	$\text{Cu}(\text{OH})_2 \cdot 2\text{CuCO}_3$
Cuprite	Cu_2O (in all copper deposits)
Enargite	Cu_3AsS_4

The sulfide ores of copper are the most abundant. Chalcocite is the most important copper ore in America. This ore is probably responsible for about half of the world's supply of copper, while it is estimated that chalcocite and chalcopyrite together yield about three-fourths of the world's production.

The world's annual production of copper is normally about one million tons, of which the United States furnishes more than half, the four leading states being Arizona, Montana, Michigan, and Utah. Much copper is also produced in Nevada, New Mexico, Alaska, California, and Tennessee. The average yield of copper from domestic ore in 1918 was 1.51 per cent. In 1906 it was 2.5 per cent. In 1914 the domestic smelter output was 1,150,137,000 pounds, while in 1918 it was 1,908,534,000 pounds. About one-tenth of our entire copper production is in the Butte district, Montana. In 1926, the production was 1,740,000,000 pounds, valued at over \$243,000,000.

Large quantities of copper are also produced in Chile, Peru, Japan, Mexico, Canada, Spain, Germany, Australia, and Russia. Valuable deposits also occur in the Katanga district of the Belgian Congo (see Radium).

The value of the copper produced in the United States in 1918 was \$471,400,000, while that produced in 1917 was \$515,000,000. Copper, therefore, ranks next to iron in value, *i.e.*, of the metals.

The amount of the metal produced in 1918 was abnormally large on account of the war. For the same reason the value was very great for the years 1917-1918.

516. Metallurgy. — In general, the production of copper pure enough for commercial purposes requires three distinct operations: namely, (1) *mining*, (2) *smelting*, and (3) *refining*. In the case of native copper, however, these three operations are not entirely distinct.

(I) **Production of copper from the native metal.** The native metal is ground, washed, and heated with a suitable flux to remove gangue.

(II) The oxide and carbonate ores are first roasted, if necessary, and then reduced by heating with carbon.

(III) The production of copper from sulfide ores is complicated, for the ores contain sulfur, iron, etc. The richer ores are subjected to direct smelting, and are known as direct smelting ores. The average yield of copper from such ores in 1918, in the United States, was 4.51 per cent. The low-grade ores require concentrating, and this is done on a large scale by the flotation process. The average yield of copper from "concentrating ores" in 1918 was, in the United States, 1.18 per cent. The flotation process has made it possible to utilize very low-grade ores and also "tailings."

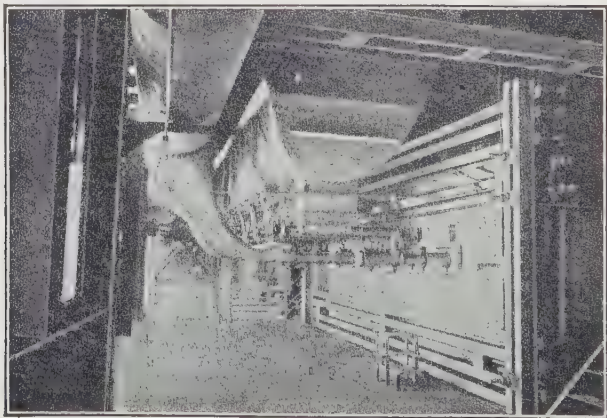


FIG. 164. Coal Dust Firing of a Reverberatory Furnace — Anaconda Reduction Works.

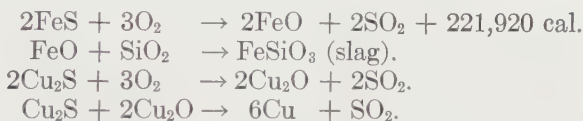
The smelting of a sulfide ore of copper (as carried out, for example, in the Butte district) is, in outline, as follows:

(1) *The ore is roasted to remove about 80 per cent of the sulfur.* Once the roasting is started, no fuel is required. The charge is heated to redness, but not melted.

(2) *The roasted ore is treated to obtain a matte.* The heated material is introduced into enormous furnaces of the reverberatory type, some of which are 100 feet by 20 feet. These furnaces are lined with silica brick and have floors of magnesite. By means

of compressed air powdered coal is blown in (see Fig. 164) and limestone is added. A large part of the iron passes into the slag and a molten mixture of sulfides of copper and iron is obtained, which is known as a **matte**. It contains 40–50 per cent of copper.

(3) *The matte (65 tons or so) is introduced into a Bessemer-like converter, and a blast of air and sand is blown through the molten mass for several hours.* The sulfur is oxidized to sulfur dioxide, the iron oxide unites with silica to form a slag, while the cuprous sulfide and oxide interact to form copper:



The product is cast in large plates, which are called **blister copper**. This form of copper usually contains from 1 to 3 per cent of impurities.

The flow of material from ore cars to copper cars is shown in Fig. 165.

517. **Refining of Blister Copper.** — For many purposes copper must be relatively pure; therefore blister copper must be refined. Blister copper is cast in ingots each of which weighs several hundred pounds. These are arranged as anodes in electrolytic tanks, while the cathodes are thin sheets of pure copper, each anode being arranged opposite a cathode. The electrolyte is a solution of cupric sulfate and sulfuric acid. A properly regulated current is passed through, and copper is carried from the anode to the cathode where it is deposited. Certain impurities pass into solution, while others, such as silver and gold, collect on the bottom of the tank as a mud (slime) which is worked over for the precious metals. Selenium, tellurium, and other by-products are sometimes obtained in the refining of copper. A representative electrolytic copper contains from 99.94–99.98 per cent of the metal. The “cathode copper” is melted and cast in commercial shapes, such as wire bars, ingots, etc.

Some of the copper from the converters is refined into anodes before it is sent to the electrolytic refining plants. This treatment is carried out in refining furnaces, which are similar to reverberatory smelting furnaces but smaller. Liquid copper from the converters or from melted slabs is treated with powdered coal and air, the remaining sulfur and iron being oxidized, and the latter

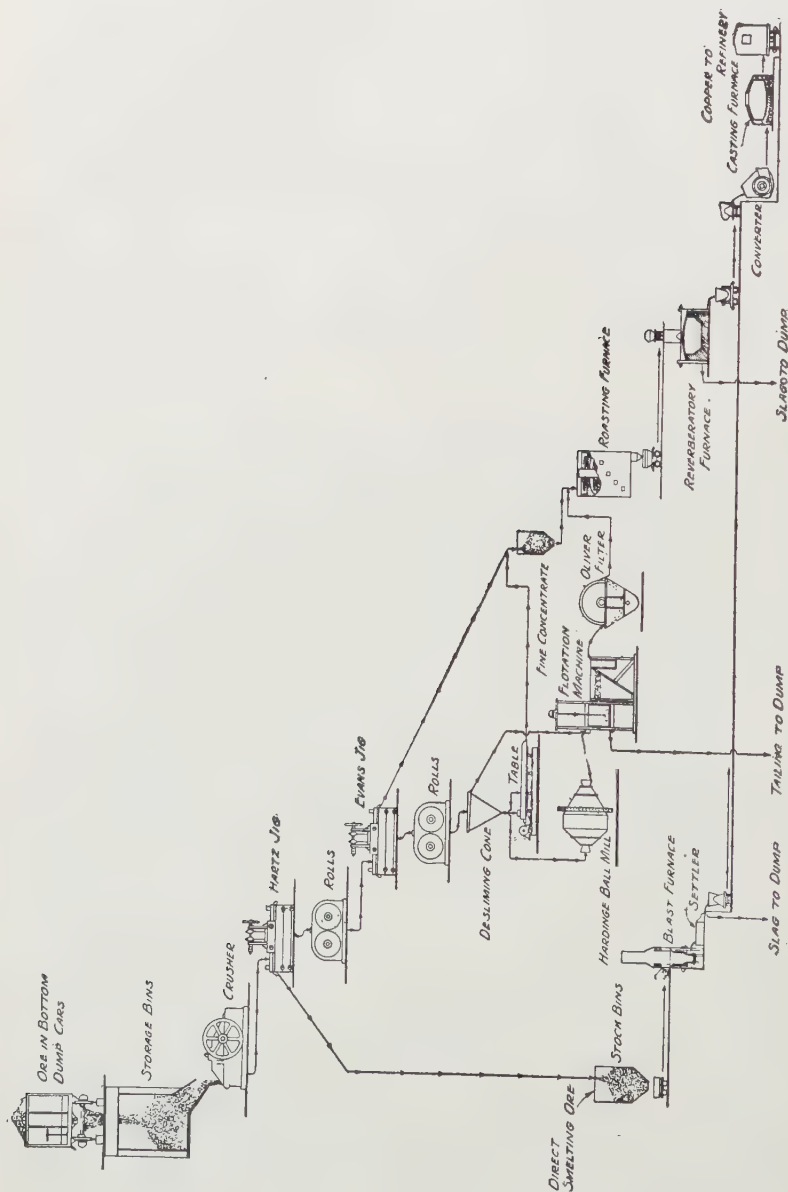


Fig. 165. The "Flow" of Material from Ore Cars to Copper Cars.

entering into the formation of slag. Any copper undergoing oxidation is reduced by means of green poles held beneath the surface of the charge. The gases from the wood reduce the cuprous oxide (Cu_2O) to copper. The metal is then cast in the form of anodes and sent to the electrolytic plant for further refining.

The lifting of cathodes out of the tanks is shown in Fig. 166.

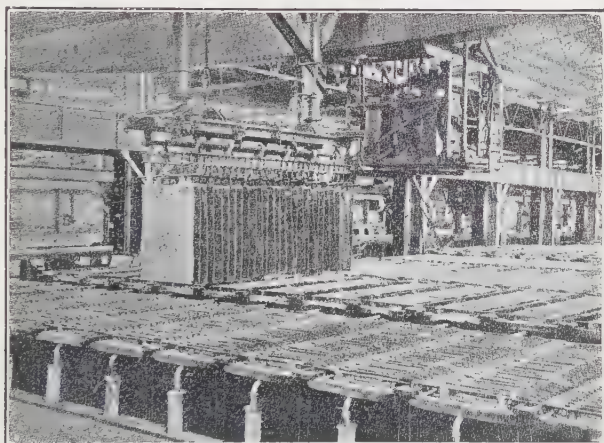


Fig. 166. Lifting Cathodes out of Tank — Raritan Copper Works.

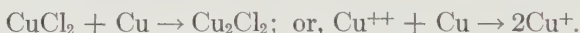
518. **Properties and Uses.** — Copper is red by reflected light and greenish by transmitted light. Its melting point is $1,083^\circ$ and its density 8.93. It is one of the most malleable and ductile of metals. Copper is slowly corroded on exposure to air, a coat of green basic carbonate being ultimately formed. The metal is soluble in nitric acid, and in hot concentrated sulfuric acid.

Copper is used very extensively in the manufacture of wire (conductors, etc.), vessels of various types, stills, roofs, bottoms of ships, and alloys: *e.g.*, brass and bronze. **Brass** is essentially an alloy of copper and zinc, containing from 18–40 per cent of the latter; it is harder and stronger than either copper or zinc, and works much better in a lathe. It is used in the manufacture of sheets, tubes, cartridges, etc. **Bronze** is ordinarily copper alloyed with tin, as well as with zinc and lead (Cu 88 per cent, Sn 8, Zn 2, Pb 2). The percentage of the metals in bronze may vary considerably. The alloy makes strong valves and fittings. **Aluminium bronze** commonly contains 90 per cent of copper and 10

per cent of aluminium; it is hard, non-corrodible, and ornamental. **Silicon-bronze** contains not more than 5 per cent of silicon. While it has about only 60 per cent of the conductivity of pure copper, it is much more tenacious, being employed for telephone and overhead electric wires. **Phosphor-bronze** contains tin and phosphorus, in addition to copper, and finds employment in certain parts of machinery. **Manganese-bronze** contains 30 per cent of manganese; propellers of ships are made of it. **Bell-metal** (bells, gongs) contains 75–80 per cent of copper and 25–20 of tin. **Gun-metal** contains 88 per cent of copper, 10 of tin and 2 of zinc. **German-silver** (Cu, Ni, Zn) is another useful alloy. Copper is used in coinage and in electrotyping.

COMPOUNDS OF COPPER

519. **Cuprous Compounds.** — These compounds may be prepared by reducing a cupric salt. Thus, cuprous chloride (Cu_2Cl_2) is prepared by boiling a solution of cupric chloride with copper:



Cuprous salts are more stable at higher temperatures than are the cupric salts, while in the presence of moisture and air the latter are more stable. Cuprous compounds are generally sparingly soluble in water, and are active reducing agents. Solutions of cuprous salts are colorless.

Cuprous oxide, Cu_2O , occurs as the mineral *cuprite*, or the red oxide of copper, sometimes called “ruby copper.” It is an important copper ore in New Jersey and elsewhere. Cuprous oxide may be formed by reducing cupric compounds.

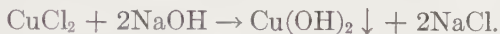
Cuprous chloride, Cu_2Cl_2 , is a white solid, soluble in concentrated hydrochloric acid and in ammonia water, forming complex compounds. These solutions are used as absorbents for certain gases, such as carbon monoxide, oxygen, and acetylene.

CUPRIC COMPOUNDS

520. **Cupric Oxide and Cupric Hydroxide.** — **Cupric oxide**, CuO , is formed by heating copper powder or turnings in the air. It occurs as the mineral *tenorite* or *melaconite*, which is not as common as cuprite. The compound is black, insoluble in water, but soluble in acids, forming cupric salts. It is a good oxidizing

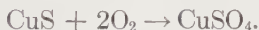
agent, for it readily parts with oxygen when heated with hydrogen, carbon, or carbon compounds. Cupric oxide is used in large quantity for removing sulfur from petroleum.

Cupric hydroxide, $\text{Cu}(\text{OH})_2$, is formed as a blue, gelatinous precipitate by treating a solution of a cupric salt with caustic soda or potash:

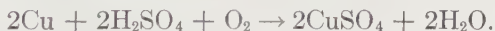


The compound is not strongly basic, and is easily decomposed by heat, forming cupric oxide. Cupric hydroxide dissolves in ammonium hydroxide to form a blue solution containing $\text{Cu}(\text{NH}_3)_4(\text{OH})_2$, which is used to dissolve cellulose in the manufacture of rayon (751).

521. Cupric Sulfate, CuSO_4 . — This is the most important salt of copper, being used on a large industrial scale. It is obtained in the refining of silver and by the oxidation of sulfides containing copper:

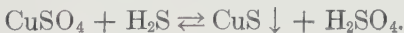


The salt also is prepared by dissolving granulated copper in dilute sulfuric acid in the presence of air:



Cupric sulfate, under ordinary conditions, crystallizes with five molecules of water, forming *blue vitriol* or *bluestone*, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. When heated it loses its water of hydration, forming the anhydrous salt CuSO_4 , which is white. Cupric sulfate is used in electroplating, the refining of copper, calico printing, as a germicide, insecticide and fungicide, and in preparing other copper compounds. *Bordeaux mixture* is prepared by dissolving blue vitriol in water and then adding calcium hydroxide, which precipitates $\text{Cu}(\text{OH})_2$; it is used extensively in spraying vegetation. Copper sulfate is sometimes employed to kill algae in water supplies; also, seeds of cereals, before planting, may be treated with a dilute solution of the salt to prevent the growth of fungi, known as smuts.

522. Other Cupric Compounds. — **Cupric sulfide**, CuS , is obtained as a brownish-black precipitate by treating a solution of a cupric salt with hydrogen sulfide:



The compound is practically insoluble in water, very sparingly soluble in dilute acids, but readily soluble in hot strong nitric acid:



The normal carbonate of copper is not known, but the **basic carbonate** occurs in nature as the minerals *malachite* and *azurite*. Beautiful specimens of malachite of the banded variety occur in Russia; it is employed as an ornamental stone. When a solution of cupric salt is treated with sodium carbonate, a basic carbonate is formed, due to hydrolysis.

Cupric nitrate, $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, is a blue, soluble, deliquescent solid.

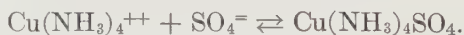
Paris Green, $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{Cu}_3(\text{AsO}_3)_2$, is used as a poison for insects: *e.g.*, the potato-beetle; it is a double salt.

Verdigris, $\text{Cu}_3(\text{OH})_2(\text{C}_2\text{H}_3\text{O}_2)_4$, is basic cupric acetate; it is prepared by exposing copper to acetic acid in the presence of air:



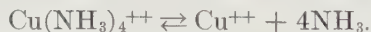
It is a green pigment, but on account of being poisonous is not extensively used as such.

When a solution of a cupric salt is treated with an excess of ammonium hydroxide, an intense azure-blue solution is obtained, on account of the formation of a complex ammonia compound: *e.g.*, $\text{Cu}(\text{NH}_3)_4\text{SO}_4$. The blue color is produced by the complex ion $\text{Cu}(\text{NH}_3)_4^{++}$:



Such salts are called **ammino salts**.

The blue ion, $\text{Cu}(\text{NH}_3)_4^{++}$, is but slightly dissociated in solution:



Owing to the very low solubility-product (254) of cupric sulfide, it fails to dissolve in ammonium hydroxide.

523. Electrotypes. — A copper electrotype, for example of a page of type, is made by preparing a plaster of Paris, wax, or gutta percha cast of the type, after which it is coated with graphite to render it a conductor, and is then employed as cathode in an electrolytic cell, which contains a solution of cupric sulfate. When the deposit of copper is stripped off, it shows an exact reproduction of the type, engraving, etc. The electrotype, before use in printing, is strengthened and thickened by filling the back with melted lead.

SILVER. $\text{Ag} = 107.88$

524. **Occurrence.** — Silver occurs native, usually being scattered through rocky matrix; it generally contains copper and gold, and native copper contains silver. Considerable masses of native silver have been found. Thus, in the museum at Copenhagen there is a mass of the metal weighing a quarter of a ton; also, masses of silver have been found in South Peru, which weigh more than 800 pounds.

The most important ores of silver are the following:

Argentite, or silver glance.....	Ag_2S
Pyrargyrite, or ruby-silver.....	Ag_3SbS_3
Stephanite, or brittle silver.....	Ag_5SbS_4
Proustite, or light ruby-silver.....	Ag_3AsS_3
Cerargyrite, or horn-silver.....	AgCl

The silver ores are associated with many other minerals: thus, much silver occurs in the mineral galena (PbS).

In 1913 the *world's production of silver* was 225,400,000 fine ounces, while in 1918 it was 197,395,000. In 1913 the value of the silver was about \$136,154,000, while in 1918 it was \$194,327,000. In 1926 the United States produced 62,718,746 troy ounces, valued at \$39,136,497.

In 1918 the United States and Canada produced about 45 per cent of the world's supply, against 57 per cent in 1917. The United States and Mexico lead in the production of silver, followed in order by Canada, Australia, Peru, and Japan.

525. **Metallurgy.** — A large part of our silver is obtained as a by-product in the refining of copper and lead. Our chief lead ore is *galena* (PbS), which often contains considerable quantities of silver sulfide, Ag_2S . Lead may be desilvered by the **Parkes process**, which makes use of the law of partition. The silver-bearing lead is melted with a small quantity of zinc, which rises to the top, carrying almost all the silver with it. On cooling, the zinc solidifies before the lead. By removing the solid and subjecting it to distillation, the more volatile zinc is expelled, leaving silver, which may be purified by **cupellation**, *i.e.*, by heating it in cupels of bone-ash. The remaining lead is oxidized to litharge, PbO , which is partly absorbed by the bone-ash. Gold contained in silver obtained by the Parkes process is recovered by an electrolytic method. Plates of the silver-gold alloy constitute the anodes, a solution of silver nitrate being employed as electrolyte. Silver is more active than gold, so it forms ions which are discharged at

the cathode. The less active gold is collected in a bag surrounding the anode.

According to modern practice, the silver ore is usually leached with sodium cyanide (see Cyanide Process, 485). Air is necessary in carrying out the leaching.



Courtesy, Department of Mines, Ontario.

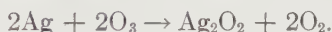
Crystals of Native Silver.

Some silver is also produced by *amalgamation*, which is applicable to ores containing free silver, or to silver chloride. The crushed ore is treated with mercury and the amalgam then heated in an iron retort, the volatile mercury being expelled. Mercury first displaces silver from silver chloride, and then forms an amalgam with it:



526. Properties and Uses. — Pure silver is a white, lustrous crystalline metal, very malleable and ductile, and capable of taking a high polish. Silver sheet 1/10,000 of an inch thick has been prepared. The melting point is 961° and the density 10.5. Molten silver absorbs about 22 times its volume of oxygen, which escapes as the metal solidifies, giving rise to the phenomenon of "spitting." Silver conducts heat and electricity better than does copper. As silver is a soft metal, it is alloyed with copper to increase the hardness. Our silver coinage has a "fineness of 900," which means 900 parts of silver in 1,000. Sterling silver has a fineness of 925.

Silver does not combine directly with oxygen, even at high temperatures, but is oxidized by ozone, forming silver peroxide:



Silver combines with sulfur to form silver sulfide. Thus, when the metal is exposed to hydrogen sulfide it tarnishes quickly on account of the formation of a film of silver sulfide. "**Oxidized silver**" is made by treating silver objects with a solution of potassium hydrogen sulfide (KHS), a thin film of the sulfide being formed. Silver dissolves readily in nitric acid, forming silver nitrate; it also dissolves in hot concentrated sulfuric acid to form silver sulfate.

Silver is used in the manufacture of alloys (coinage, silverware, etc.) and mirrors, in electroplating, photography, etc. "**Frosted silver**" is made by heating a silver-copper alloy in the air until the copper near the surface is oxidized. By treating the object with sulfuric acid, the copper oxide is dissolved, leaving a superficial layer of pure silver.

SILVER COMPOUNDS

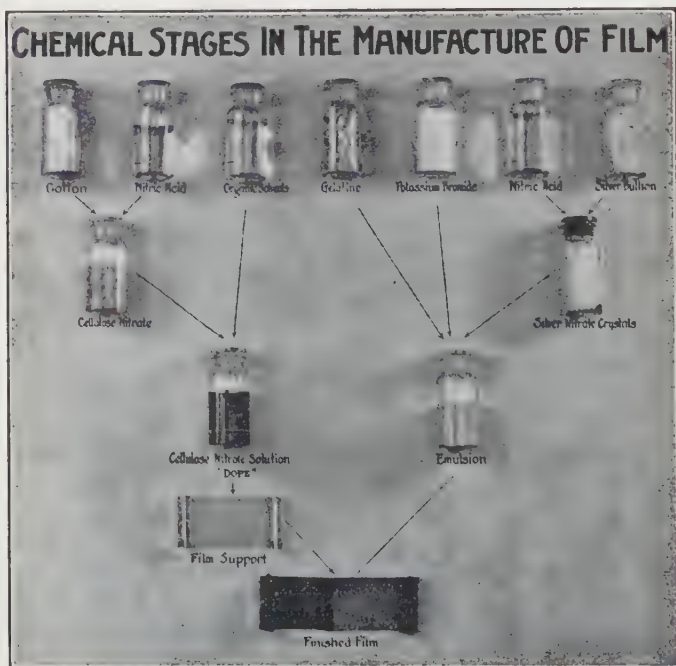
527. Silver Oxides. — When a soluble silver salt is treated with sodium hydroxide, a pale-brown precipitate is obtained. Silver hydroxide is no doubt formed, but since it is unstable, it decomposes to form the oxide Ag_2O :



The aqueous solution of silver oxide is distinctly alkaline, so silver hydroxide is regarded as a moderately active base. When the oxide is heated, it yields silver and oxygen. This action is revers-

ible (see Mercuric Oxide). Silver peroxide, Ag_2O_2 , has already been mentioned.

528. **The Halides of Silver.** — The **chloride** AgCl (white), the **bromide** AgBr (pale yellow), and the **iodide** AgI (yellow) may be obtained as curdy precipitates by treating solutions of silver salts with soluble halides. These compounds are practically insoluble



Courtesy, Eastman Kodak Co.

FIG. 167. The Manufacture of Photographic Film.

in water, but are soluble in a number of normal salts, such as sodium thiosulfate ("hypo"), forming complexes:



This property of the silver halides is turned to profit in photography and in metallurgy. In **photography** dry plates are prepared by covering glass plates or films of nitrocellulose or cellulose acetate with a coating of gelatin in which silver bromide (or iodide) is suspended, and then allowing them to dry (Fig. 167). When the plates are exposed for a very brief period to the action of light,

the silver salt, where exposed, is decomposed by the light, silver being formed. By treating the plates with certain reducing agents, called **developers** (an alkaline solution of a weak reducing agent, such as ferrous oxalate, pyrogallol, or hydroquinone), the salt which was exposed to the light is acted upon more readily; therefore an image appears, which is a black film of metallic silver. The plate is now treated with a suitable **fixing agent** (*e.g.*, sodium thiosulfate) in order to dissolve the unaffected silver salt. When the plate is washed and dried, it is called a **negative**. The preparation of the print is made from the negative. The development and fixing of positives is similar chemically to that of negatives. Prints may be toned by treating them with solutions of gold or platinum compounds. Some of the silver is displaced by the finer metal, which adds to the beauty and permanence of the photograph.

Silver fluoride, AgF , may be formed by dissolving the oxide or carbonate in hydrofluoric acid. It is extremely soluble in water, 100 g. of the latter dissolving 195.4 g. of the salt at 18° . (Contrast this with the solubility of the other halides of silver.)

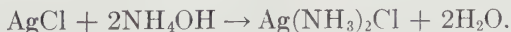
529. **Silver Nitrate** (*Lunar Caustic*), AgNO_3 . — Silver nitrate is a salt of great value. It is prepared by dissolving silver in dilute nitric acid:



It crystallizes in large rhombic plates which melt at 208.6° . The salt is very soluble in water. At 18° , 100 g. of water dissolve 213.4 g. of the nitrate; while at 100° , 910 g. of the salt dissolve. Silver nitrate is a powerful oxidizing agent, and is often cast in the form of sticks for use in surgery. When silver nitrate is brought in contact with the skin, cloth, or other organic matter, a black stain is produced, because of the reduction of the salt to metallic silver. The salt therefore finds application in the manufacture of "marking inks" and hair dyes.

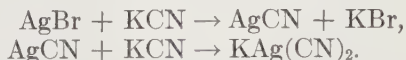
530. **Complex Compounds and Ions of Silver**. — As shown under a previous section, silver halides dissolve in sodium thiosulfate solution to form the complex compound $\text{Na}_3\text{Ag}(\text{S}_2\text{O}_3)_2$. A solution of this salt appears to contain the ion $\text{Ag}(\text{S}_2\text{O}_3)_2^{=}$.

Silver chloride dissolves in ammonium hydroxide, forming ammonio-silver chloride:

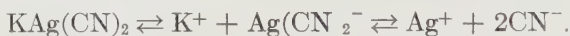


The salt yields the **ammonio-silver ion** $\text{Ag}(\text{NH}_3)_2^+$.

When a solution of a silver salt or a halide of silver is treated with potassium cyanide, insoluble silver cyanide (AgCN) is first formed, which dissolves in excess of the reagent, forming **potassium silver cyanide**, $\text{KAg}(\text{CN})_2$:



This silver salt is employed in **electroplating**. The article to be plated is the cathode, a plate of silver is the anode, and a bath of potassium silver cyanide serves as electrolyte. The complex silver salt ionizes thus:



A very low concentration of the silver ion is present, but when it is discharged, more of the complex ion is formed. The following change occurs at the cathode:



The potassium-ion is not discharged, for potassium requires a much higher E.M.F. for its liberation than does silver.

In this connection it is of interest to note that **silver mirrors** may be produced by treating well-cleaned glass with a suitable silver compound. For this purpose the silvering solution generally contains silver nitrate, slight excess of ammonia, and an organic reducing agent, such as a tartrate, glucose, or an aldehyde.¹ In certain cases the silver solution is warmed.

531. Other Silver Compounds. — **Silver sulfide**, Ag_2S , may be obtained as a black precipitate by treating solutions of silver salts with hydrogen sulfide; it is practically insoluble in water and in dilute acids, but soluble in strong nitric acid.

Silver sulfate, Ag_2SO_4 , is sparingly soluble in water. It may be prepared by dissolving silver in concentrated sulfuric acid (see Copper and Sulfur Dioxide).

¹ Excellent results may be secured by employing the following solutions:

Solution No. 1. — 10 g. of silver nitrate are dissolved in a small quantity of water, and ammonium hydroxide is added carefully, with stirring, until the precipitate which first forms just dissolves. The solution is then filtered, and diluted to one liter.

Solution No. 2. — 2 g. of silver nitrate are dissolved in a liter of pure, boiling water, followed by the addition of 1.66 g. of Rochelle salt ($\text{KNaC}_4\text{H}_4\text{O}_6$). The solution is then filtered.

Just before use for silvering glass, mix equal volumes of the two solutions.

Silver chromate, Ag_2CrO_4 , is a red solid, and but slightly soluble in water.

Silver phosphate, Ag_3PO_4 , is a yellow solid, practically insoluble in water.

Silver arsenate, Ag_3AsO_4 , is a brown solid, insoluble in water, but soluble in nitric acid.

GOLD. Au = 197.2

532. **Occurrence.** — Gold occurs largely in the native condition, hence it was one of the first metals used by man. The metal is mentioned in ancient writings, the earliest words for the metal in Hebrew and in Egyptian referring to its shining appearance. The ancients considered it to be the noblest of metals. Flint daggers with gilt handles have been found in Egyptian excavations, and gold was coined several hundred years B.C. Free gold is not abundant, but is widely distributed. The metal is disseminated in veins of quartz, and is usually associated with other metals, such as silver, copper, or iron; it also occurs mixed with alluvial sand and gravel. Many minerals, such as iron pyrites, galena, and zinc blende, contain very small quantities of gold. Gold also occurs as the mineral *sylvanite* ($\text{Au Ag})\text{Te}_2$, a telluride found in Colorado.

The world's production of gold in 1913 was valued at \$460,500,000, and in 1918 at \$381,000,000 — a decrease of \$79,500,000. The world's production of gold from 1860-1918 is valued at nearly thirteen billion dollars. Africa leads in the production of gold. The Rand deposits are especially rich; in 1919 the Transvaal produced about two-fifths of the world's output. The United States, Mexico, Canada, Australasia, Russia, and India, are large producers of gold. The chief deposits of the metal, apart from those of South Africa, follow the Pacific Ocean. In 1926 the United States produced 2,335,042 troy ounces, valued at \$48,269,600.

Gold is the basis of international credit, the price remaining stationary, namely, \$20.67 per ounce.

533. **Metallurgy.** — Gold is produced by several different processes. The gold found in alluvial deposits may be separated from gangue by washing in a pan ("cradling" or "panning"). This is a very primitive method, being used mainly by the prospector. The lighter earthy matter is washed over the edge of the pan.

"Placer mining" consists in washing the material through a sluice box. On account of its high density gold settles to the bottom and the lighter material is washed away. In "hydraulic

mining" a powerful stream of water is employed to wash the gold and earthy matter into the sluices.

The **amalgamation process** may be employed to catch the particles of gold which escape through the sluices. The dirt and gold leaving the sluices are washed over amalgamated copper plates or cleats. By heating the gold amalgam, mercury is volatilized.

The cyanide process is the chief one used for gold (485). This is similar to the cyanide process for silver. It is applicable to very low-grade ores and "tailings," and it has increased the production of gold enormously since its introduction in 1890, particularly in South Africa. It is reported that the United States consumed in 1918 about 1,900 tons of cyanides in extracting gold and silver, practically all of which was sodium cyanide. The cyanide process is used on a large scale in Nevada.

Gold may be purified by electrolysis or by cupellation. It may be separated from silver and many other metals by heating the alloy with strong sulfuric acid, the gold being insoluble.

534. Properties. — Gold, in the massive state, is a yellow, shining metal; but if it be precipitated in a finely divided condition, *e.g.*, by the addition of ferrous sulfate to a solution of the chloride, the metal has a brownish color by reflected light. Gold leaf by transmitted light possesses a green or blue color. Its melting point is $1,063^{\circ}$ and the density is 19.32. Gold is the most malleable and ductile of metals. The metal can be deposited in extremely thin layers: *e.g.*, the deposit on gold lace is about 0.000002 mm. thick! The metal is soft, so it must be alloyed with copper and other metals to increase its hardness. American, French, and German coins contain 10 per cent of copper and 90 per cent of gold (21.6 carat), while the British sovereigns are 22 carat.

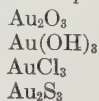
Only a few chemical reagents attack gold. It is attacked, however, by fused alkalies and nitrates and by phosphorus, and dissolves in *aqua regia* to form chlorauric acid, HAuCl_4 (or $\text{HCl} \cdot \text{AuCl}_3$); it is dissolved by liquids containing free chlorine or bromine, and by solutions of the alkali cyanides in the presence of air. Gold is much more resistant than are copper and silver.

535. Compounds of Gold. — The metal forms *aurous* and *auric* compounds, in which the valence is one or three:

Aurous Compounds



Auric Compounds



Chlorauric acid, HAuCl_4 , formed by dissolving gold in *aqua regia*, is one of the most important compounds of gold. Its sodium salt, $\text{NaAuCl}_4 \cdot 2\text{H}_2\text{O}$, finds use as a toning reagent in photography. When the acid is heated, it yields auric chloride:



Auric chloride is a red crystalline solid, which is readily soluble in water. When heated to 180° , it gives *aurous chloride* (white) and chlorine. At a higher temperature aurous chloride decomposes into gold and chlorine:



Gold, like copper and silver, can be precipitated as sulfides by hydrogen sulfide. *The sulfides of gold are soluble in alkali sulfides* (see Tin, Arsenic, and Antimony).

The compounds $\text{KAu}(\text{CN})_2$ and $\text{KAu}(\text{CN})_4$ are employed as electrolytes in electro-gilding. In general, gold compounds are unstable at high temperatures and are readily reduced.

536. Analytical. — When a solution containing the ions of copper (Cu^{++}), silver (Ag^+), and gold (Au^{+++}) is treated with dilute hydrochloric acid, the silver is precipitated as the chloride AgCl , which is white and curdy and turns dark on exposure to light. Silver chloride is soluble in ammonium hydroxide, forming ammonio-silver chloride, $\text{Ag}(\text{NH}_3)_2\text{Cl}$. When nitric acid is added to this solution, silver chloride is reprecipitated.

When hydrogen sulfide is added to a cold, slightly acid solution containing Cu^{++} and Au^{+++} , the metals are precipitated as sulfides. Cupric sulfide is black and is insoluble in ammonium sulfide (see Tin, Arsenic, and Antimony), but is soluble in hot dilute nitric acid. On adding ammonium hydroxide in excess to a solution of a cupric salt, an azure-blue solution is obtained, due to the formation of the complex ion $(\text{Cu}(\text{NH}_3)_4)^{++}$.

Gold sulfide is black; it is insoluble in such an acid as nitric or hydrochloric, but readily soluble in *aqua regia*, forming auric chloride (AuCl_3).

The formation of *purple of Cassius* affords a characteristic test for the presence of gold. This test can be made by warming a solution containing stannous chloride and stannic chloride with a very dilute solution of gold salt, whereupon the gold is reduced by the stannous chloride, and a precipitate of gold and stannic acid is obtained.

EXERCISES

1. Show the relation of the metals of the copper family to the alkali metals and to mercury. Give the general characteristics of the metals of the copper family.

2. The analogues of silver are palladium, cadmium, copper, and gold. Explain.

3. Give the occurrence of copper, including the names and formulae of its chief ores. Which are the most common and abundant?

4. Outline the metallurgy of copper as it relates (1) to native copper; (2) cuprite, malachite, or azurite; and (3) to the sulfide ores. How may a low-grade copper ore be concentrated? What is a copper "matte," and how may copper be obtained from it? What is "blister copper"?

5. Explain fully from the standpoint of the ionic theory the electrolytic refining of copper. What important by-products are obtained?

6. Give the general characteristics of cuprous and cupric compounds. How would you prepare the following compounds: Cu_2O , CuO , $\text{Cu}(\text{OH})_2$, Cu_2Cl_2 , CuCl_2 , and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$? Mention some of the uses of copper compounds.

7. How would you separate copper from calcium? How may cupric salts be identified? Explain why $\text{Cu}(\text{OH})_2$ is soluble in ammonium hydroxide.

8. Give the occurrence of silver. With what metals is silver commonly associated?

9. Outline the following processes for the production of silver: (1) the cyanide process; (2) Parkes' process; and (3) the amalgamation process. How would you prepare silver of a very high degree of purity? How would you obtain the metal from silver chloride?

10. State the properties of silver. Explain the electro-deposition of silver from a cyanide solution. How would you silver a mirror or a glass tube?

11. How may the halides of silver be prepared? Explain why silver chloride is soluble in ammonium hydroxide and in potassium cyanide. Outline the photographic process.

12. Give the preparation, properties, and uses of silver nitrate. Write chemical equations to show the formation of the following compounds, and state two properties of each:



13. How would you determine the percentage of silver in a silver coin? How may silver be "oxidized," and a silver-copper alloy "frosted"?

14. Give the occurrence of gold. Mention five countries which lead in the production of the metal.

15. Outline the metallurgy of gold. Explain why the output of gold has increased so rapidly since 1890. Why has the output decreased in recent years?

16. Compare the properties of gold with those of platinum.

17. Compare the electrical conductivity, malleability, ductility, and tenacity of gold and copper.

18. How would you bring about the chemical union of gold with chlorine? with oxygen? Are any of the gold compounds stable at high temperatures?

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CHAPTER XXX

THE ALKALINE EARTH METALS

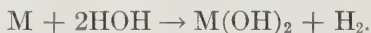
537. General Characteristics. —

Element	Atomic Weight	Atomic Number	Density	Melting Point
Calcium, Ca	40.07	20	1.55	810°
Strontium, Sr	87.63	38	2.54	900°
Barium, Ba	137.37	56	3.8	850°
(Radium, Ra)	226.00	88	700°

The oxides of these metals were originally called the alkaline earths on account of their resemblance to the alkalis and to the oxides of the earths (*e.g.*, those of aluminium and of iron). Radium is a member of this family, but owing to its unusual properties and its relation to uranium it is considered in a separate chapter (IV).

All the alkaline earth elements are bright, silvery, soft, malleable metals, but are harder, denser, and less fusible than are the alkali metals. In their chemical properties they are closely related to the alkali metals, but are, in general, less active. Magnesium and beryllium are related to the alkaline earth metals, but are more closely related to zinc; they may be regarded as linking the alkaline earth metals to the zinc group.

Calcium, strontium, and barium are very closely related, their chemical activity increasing with increasing atomic weights. They are bivalent and form such compounds as MO , $\text{M}(\text{OH})_2$, MH_2 , M_3N_2 , $\text{M}(\text{NO}_3)_2$, etc. They interact readily with cold water to form hydrogen:



When heated, they burn in air to form oxides of the type MO (mixed with nitride). The hot metals also unite with hydrogen to form hydrides, and with nitrogen to form nitrides. They tarnish, when exposed to the air, but not so quickly as do the

alkali metals. The oxides dissolve in water to form active bases:



The solubility of the hydroxide increases with the atomic weight of the element. The hydroxides are decomposed by heat, whereas the hydroxides of the alkali metals are very stable. The carbonates are virtually insoluble in water and are decomposed at a high temperature, BaCO_3 being the most difficult to decompose:



The bicarbonates are soluble and unstable. The nitrates are also decomposed by heat:



They are less stable than are the nitrates of the alkali metals. The solubility of the sulfate in water decreases with increase in atomic weight of the metal, only 2.3 parts of BaSO_4 being soluble in 1,000,000 parts of water at 18° .

When the fused chloride or hydroxide is subjected to electrolysis, the free metal is obtained. The metals can also be isolated by reducing their halides by sodium or potassium. The metals are not used on a large scale, however.

They form carbides of the type MC_2 , which readily interact with water to form hydrocarbons, mainly acetylene (C_2H_2):



They form peroxides (MO_2), but only in the case of barium is the peroxide formed by heating the oxide in air.

CALCIUM. Ca = 40.07

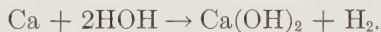
538. Occurrence. — Calcium constitutes nearly 3.5 per cent of the earth's crust, being a constituent of many important minerals and rocks. By the weathering and decomposition of rocks calcium finds its way into natural waters, to which it imparts "hardness." Calcium occurs very abundantly as the carbonate, CaCO_3 . Limestone, marble, calcite, chalk, and sea-shells are familiar forms of calcium carbonate. When waters containing magnesium salts percolate through calcium carbonate, calcium may be partly displaced by magnesium, forming dolomite, $\text{CaCO}_3\text{-MgCO}_3$. Calcium also occurs abundantly as hydrated calcium

sulphate, or gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, and as anhydrite, CaSO_4 . The phosphate $\text{Ca}_3(\text{PO}_4)_2$ is found in natural deposits and in bones; fluorspar, CaF_2 , is another important calcium mineral. It may be colored blue or red, due, perhaps, to traces of impurities.

539. Preparation and Properties. — Calcium (Lat. *calx*, lime) was first obtained by Davy, in 1807, by the electrolysis of fused calcium hydroxide. *It is now prepared by electrolyzing the fused chloride to which calcium fluoride may be added to lower the melting point.* The electrolysis is conducted in a graphite crucible which serves as anode, an iron ribbon or rod being employed as cathode. The calcium adheres to the cathode, which is gradually raised, and a rod of the metal is built up in the form of a "cabbage-stalk."

Calcium is a silvery white metal, which turns slightly yellowish on exposure to the air, due to union with nitrogen. When heated in air, it burns to form a mixture of oxide and nitride. Its density is 1.55 and it fuses at 810° ; it is malleable and is a little harder than lead.

Calcium is an active metal and strongly electropositive in character, but less so than are the alkali metals. The metal combines directly with hydrogen, oxygen, nitrogen, the halogens, sulfur, and carbon; it readily decomposes cold water:



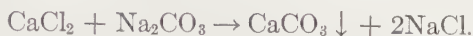
The solid, **calcium hydride** (CaH_2), obtained by heating the metal with hydrogen, is known commercially as **hydrolite**; it is a source of hydrogen for military purposes, but is rather expensive.

Metallic hydrides have the characteristics of salts. Bardwell has succeeded in electrolyzing calcium hydride, hydrogen being obtained at the anode in amount corresponding to the law of Faraday (229).

COMPOUNDS OF CALCIUM

540. Calcium Carbonate, CaCO_3 . — As previously stated, calcium carbonate occurs very abundantly in nature. The mineral calcite or Iceland spar crystallizes in the hexagonal system, and aragonite in rhombic prisms. **Limestone** is essentially calcium carbonate, but it contains more or less foreign matter, such as magnesium carbonate, clay, silica, and compounds of iron. Pearls, coral, and many kinds of shells and natural chalk are largely calcium carbonate. **Marble** is crystalline limestone. Carrara marble is noted for its purity and whiteness. **Marl** is a mixture of limestone and clay.

Calcium carbonate may be prepared in the laboratory by the interaction of aqueous solutions of calcium chloride and sodium carbonate:



The compound is virtually insoluble in pure water, but soluble in water containing carbon dioxide, forming the bicarbonate, $\text{Ca}(\text{HCO}_3)_2$, which renders water temporarily hard (148). When heated to a high temperature, it decomposes with the formation of calcium oxide and carbon dioxide. It is soluble in acids, giving carbon dioxide.

Calcium carbonate is used in enormous quantities. Limestone is employed as building stone, crushed stone, fluxing stone, in alkali works, sugar factories, agriculture, and in the manufacture of glass. Large quantities of marble are also used.

541. **Calcium Oxide and Hydroxide.** — Calcium monoxide or "quicklime," CaO , is manufactured on a very large scale by heating limestone in kilns (Fig. 168):



Both continuous and intermittent kilns are employed, but the former type is more economical. To produce a lime free from ash, the fires are built at the sides of the kiln, the gases passing up through the kiln, the lime being removed at the bottom. This is known as the "long-flame" process. In the "short-flame" process a mixture of limestone and fuel is heated in the kiln; the product contains ash. Much lime is now produced in rotary kilns very similar to those employed in the manufacture of cement.

When calcium carbonate is heated the reaction is reversible, so the heating of limestone must be carried out under such conditions as favor the dissociation of the carbonate. This is accomplished by means of high temperature and by expelling the carbon dioxide. If the dissociation of the carbonate were carried out in a closed vessel, equilibrium between the opposed actions would be reached at a definite temperature and the action

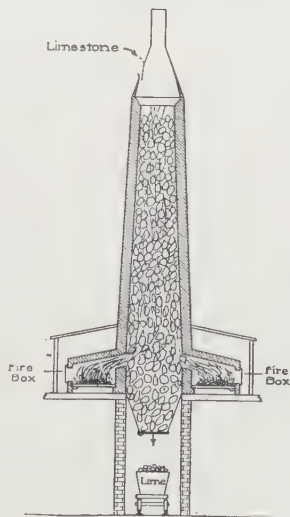


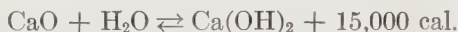
FIG. 168.

would not be completed. The pressures in millimeters of mercury at several different temperatures are as follows (John Johnston):

Temperature (C.)...	587°	701°	748°	840°	894°	898°
P _{CO₂} mm. Hg.....	1	23	70	311	716	760

If the carbon dioxide is removed from the kiln as fast as it is formed, the action goes forward rapidly, particularly at the higher temperatures. Too high a temperature should not be employed, for fusible silicates would be formed, which would fill the pores of the lime and interfere with the subsequent slaking. The carbon dioxide is carried away with a current of air, thus reducing its partial pressure. The quality of lime necessarily depends largely on the kind of limestone used in its manufacture.

When quicklime comes in contact with water it unites with it, producing much heat:



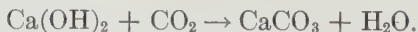
The lumps of lime crumble to a powder, forming "slaked" lime, or calcium hydroxide. When a large excess of water is added, a liquid of creamy consistency, known as "milk of lime," is obtained. Limewater is an aqueous solution of calcium hydroxide. At 0°, 100 g. of water dissolve 0.185 g. of Ca(OH)_2 ; but at 100°, only 0.077 g. dissolves. When quicklime is exposed to the air, it not only combines with water but absorbs carbon dioxide as well, forming the carbonate ("air-slaked lime").

While calcium hydroxide is sparingly soluble in water, it is our cheapest base — cheaper than caustic soda, caustic potash, or ammonium hydroxide.

Lime is infusible at the temperature of the oxyhydrogen blow-pipe, but fuses and boils at the temperature of the electric furnace, which is about 3,500°. It melts at about 2,000°.

The manufacture and use of lime can be traced back to times of remote antiquity. It is used in over 100 chemical industries, in construction work, and in agriculture. In 1926 the United States produced 4,580,000 tons of lime, valued at \$40,800,000.

Ordinary **mortar** is prepared by mixing slaked lime with quartz sand (SiO_2). The hardening of the mortar is due, in part, to the loss of water and the gradual combination of the hydroxide with carbon dioxide of the air:



It is believed that colloidal calcium hydroxide is formed, which

gradually dries and "sets" very much as does glue. Mellor says: "In the mortars of some of the buildings of the ancient Romans, crusts of minute calcium carbonate crystals protect the inner cores of calcium hydroxide. An exposure of 2,000 years has not been sufficient to convert more than thin superficial layers of the colloidal hydroxide into carbonate."

542. **Cement and Concrete.** — When certain argillaceous limestones (*i.e.*, limestones containing more than 10 per cent of clay) are heated to a high temperature in a kiln (Fig. 169) and then

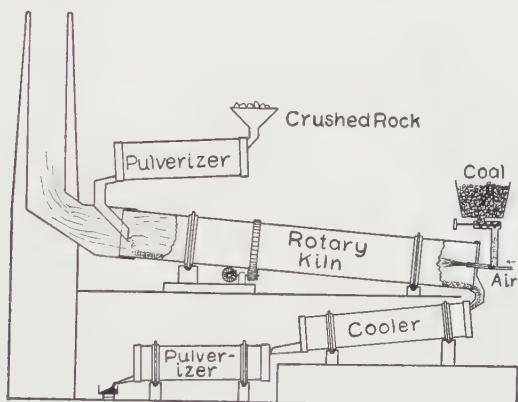
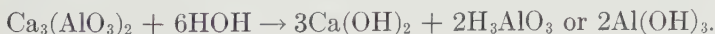


FIG. 169.

ground to a powder, they form **hydraulic cement**; for they possess the property of hardening ("setting") under water. **Portland cement** is a common variety; it resembles stone found at Portland, England. In the United States it is manufactured by heating a mixture of limestone and shale, or marl and clay, in long rotary kilns, and then grinding the "clinker." The United States produced about 71,000,000 barrels of Portland cement in 1918, nearly 23,000,000 barrels having been manufactured in Pennsylvania alone. In 1926 the production rose to 164,219,000 barrels of cement, valued at over \$280,000,000.

Cements are largely a mixture of calcium silicate and calcium aluminate, an excess of lime being present. They are usually highly basic in character. In hardening, complex reactions occur, hydration and hydrolysis both playing a part. Calcium aluminate, $\text{Ca}_3(\text{AlO}_3)_2$, is hydrolyzed as follows:



The calcium hydroxide thus formed gradually crystallizes, cementing the particles of calcium silicate, while the aluminium hydroxide fills the interstices. The cement finally becomes compact and hard.

Concrete is a mixture of cement, sand, and crushed stone or gravel, made into a paste by means of water. It is our most important building material, and is used in immense quantities in the construction of roads. Its advantages are apparent to all.

543. Calcium Sulfate, CaSO_4 . — The dihydrate, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, occurs abundantly as **gypsum**. This mineral is widely distributed. Crystalline gypsum having perfect cleavage is called **selenite**. The granular massive form of gypsum is **alabaster**, while the fibrous variety with a satiny or pearly luster is **satin spar**. **Anhydrite**, CaSO_4 , also occurs abundantly in nature: for instance, in the Stassfurt salt beds. Gypsum is used in agriculture, for the manufacture of plaster of Paris and wall plaster, and as a filler for paper. Its value as a fertilizer is attributed to its interaction with the ammonium carbonate of the soil to form ammonium sulfate, which is more stable and less volatile than is the former, and is therefore retained longer in the soil for the plants. In 1926 the United States produced 5,635,000 tons of gypsum, valued at over \$46,700,000.

Plaster of Paris $(\text{CaSO}_4)_2 \cdot \text{H}_2\text{O}$, so named from the Montmartre deposits near Paris where this cement was first produced, is manufactured by heating gypsum until about three-fourths of the water of hydration is expelled:

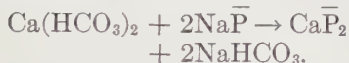


Too high a temperature must be avoided, else the product will become "dead-burnt" and will not readily set, unless the hydration is catalyzed by such a substance as alum. When plaster of Paris is mixed with water, it sets to a white solid; for the dihydrate is formed as a network of interlacing fibrous crystals. It is used for making casts and in surgery, for the finishing coat of plastered walls, for the manufacture of stucco, etc. **Keene's cement** is produced by mixing "dead-burnt" cement with a little alum. It is widely used for interior decoration in imitation of marble. **Stucco** is a mixture of plaster of Paris and rubble, together with a solution of size or glue. Alabaster and satin spar are used as ornamental stones and as inexpensive jewelry.

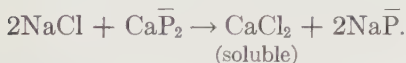
Gypsum is sparingly soluble in water, 1 part of the hydrate dissolving in about 500 of water at 18°. Water containing calcium

sulfate in solution, is said to be permanently hard; it may be softened by adding sodium carbonate (148).

The "**permutite**" process is a modern one for the softening of water. The water is filtered through permutite, an artificial sodium silico-aluminate, which is employed in the form of a coarse sand (Fig. 170). The calcium, magnesium, etc., of the hard water are exchanged for sodium. Representing permutite by the formula $\text{Na}\bar{\text{P}}$, in the case of a temporarily hard water, the chemical equation for the change may be written thus:



When the permutite has been in use for 12 hours, it is covered with a 10 per cent solution of NaCl and allowed to remain out of use for another 12 hours, after which it is ready for further employment:

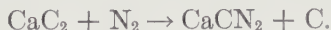


It is claimed that the life of a charge is over 20 years.

544. Other Calcium Compounds. — The *phosphates of calcium* have already been discussed (413).

Calcium carbide, CaC_2 , is produced on a large scale for use in generating acetylene and for the manufacture of calcium cyanamide (445).

Calcium cyanamide, CaCN_2 , is produced (Figs. 171–172) by passing nitrogen over calcium carbide heated to about $1,000^\circ$:



It is used as a fertilizer and in the production of ammonia and sodium cyanide:

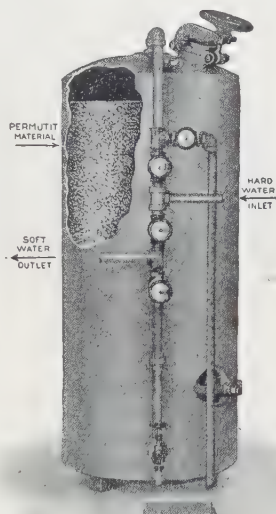
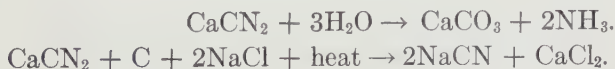
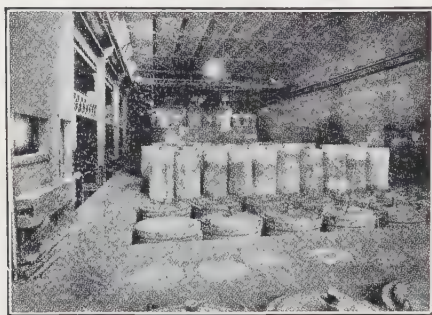


FIG. 170. Softening Water by the Permutite Process.

Calcium fluoride, CaF_2 , occurs in large quantities as the mineral fluorspar, being mined especially in Illinois and in Kentucky.



Courtesy, The American Cyanamide Co.

FIG. 171. The Manufacture of Calcium Cyanamide.

It is used as a flux and in the manufacture of opaque glass, white enamel, and hydrofluoric acid.

Calcium chloride, CaCl_2 , is obtained in immense quantities as a by-product of the Solvay process (498). It is extremely soluble in water, is very deliquescent, and is therefore used as a drying agent and for settling dust on roads. Several hydrated forms of the salt have been prepared.

A saturated solution of calcium chloride freezes at -48° ; it is used as the brine in refrigeration.

Calcium bisulfite, $\text{Ca}(\text{HSO}_3)_2$, is used in large quantities in the manufacture of paper, being a solvent for lignin (337).

Bleaching powder, CaOCl_2 , is used extensively as a bleach and disinfectant (307).

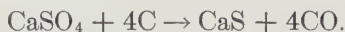
Calcium oxalate, CaC_2O_4 , is one of the most insoluble compounds of calcium. The salt occurs in many plants. It can be obtained as a white precipitate by treating a neutral or alkaline solution of a calcium salt with ammonium oxalate:



The oxalate is decomposed at high temperatures:



Calcium sulfide, CaS , is prepared by heating calcium sulfate with carbon:

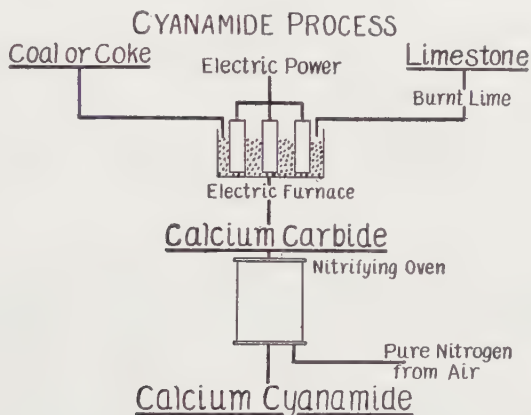


The compound is sparingly soluble in water, but is slowly hydrolyzed, forming more soluble compounds:



This explains why the metals of the alkaline earth group cannot be precipitated as sulfides.

When ordinary calcium sulfide has been exposed to sunlight, it usually shines in the dark, on account of impurities associated with the substance. For this reason it is used in the production



Courtesy, Fixed Nitrogen Research Laboratory.

FIG. 172. Diagrammatic Representation of the Manufacture of Calcium Cyanamide.

of *luminous paints*. Sulfides of strontium and barium are also phosphorescent.

Calcium compounds when volatilized in the non-luminous flame impart to it a brick-red color. Its spectrum contains several lines in the orange and yellow, one in the green, and one in the ultra-violet, the orange and green lines being particularly bright.

STRONTIUM. $\text{Sr} = 87.63$

545. **Occurrence and Properties.** — **Strontium**, from *Strontian*, a village in Scotland, occurs chiefly in the minerals **celestite**, SrSO_4 , and **strontianite**, SrCO_3 . Workable deposits of strontium ores occur in Arizona, California, Texas, Utah, and Washington. Strontianite is imported from England. Celestite is the more abundant ore, very large crystals of the mineral being found on Strontian Island, Lake Erie.

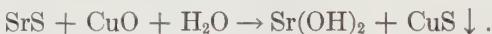
The method of preparation is the same as that for calcium. The two metals also have similar properties.

Volatile strontium salts impart a beautiful crimson color to the non-luminous flame. Its spectrum contains many lines, the most intense being an orange line, two red lines, and a blue line.

546. Strontium Compounds. — In general, the compounds of strontium closely resemble those of calcium. They are usually prepared from celestite or strontianite. Thus, celestite can be reduced to strontium sulfide by heating it with carbon:



When strontium sulfide is treated with cupric oxide and water, a solution of strontium hydroxide is formed, cupric sulfide forming an insoluble residue:



It crystallizes with eight molecules of water, $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$.

Strontium hydroxide has been useful for separating from molasses the cane sugar which cannot be obtained by crystallization, for it forms with the sugar an insoluble compound. By suspending the compound in water and passing in carbon dioxide, strontium carbonate is precipitated and sugar is left in solution. Lime is now to a large extent used instead of strontium hydroxide.

Strontium oxide, SrO , can be obtained by heating the carbonate. It is more soluble in water than is lime.

Strontium nitrate, $\text{Sr}(\text{NO}_3)_2$, is obtained by treating the oxide, hydroxide, or carbonate with nitric acid. It is readily soluble in water and is largely used in pyrotechny for red fire, flares, signal shell and lights. The salt crystallizes with four molecules of water, $\text{Sr}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$.

Strontium carbonate, SrCO_3 , may be prepared from SrSO_4 .

The transformation of strontium sulfate into strontium carbonate is an excellent illustration of the principle of **solubility-product** or **ion-product constant** (254). This may be accomplished by boiling strontium sulfate with a solution of sodium carbonate:



The reaction is reversible; but by using an excess of sodium carbonate and by boiling for some time, the transformation may be practically completed.

The solubility of SrSO_4 in water is greater than that of SrCO_3 , so the former is converted into the latter by boiling with a con-

centrated solution of Na_2CO_3 . The solubilities in water of these two salts of strontium are as follows:

	<i>Solubility in grams per liter</i>	<i>Molar solubility per liter</i>
SrSO_4	0.11	0.0006
SrCO_3	0.011	0.00007

The solubility-product of SrSO_4 , for a saturated solution, is, assuming it to be completely ionized, as follows:

$$[\text{Sr}^{++}] \times [\text{SO}_4^{=}] = \text{Constant} = 0.0006 \times 0.0006; \text{ and for } \text{SrCO}_3, \\ [\text{Sr}^{++}] \times [\text{CO}_3^{=}] = 0.00007 \times 0.00007.$$

When strontium sulfate is treated with a concentrated solution of sodium carbonate, the solution soon becomes supersaturated with respect to SrCO_3 , owing to the low ion-product constant. SrCO_3 therefore separates out and the more soluble SrSO_4 goes into solution to restore equilibrium. When the two solids are in equilibrium, the ratio of the concentrations of their anions

$$\left(\frac{\text{conc. CO}_3^{=}}{\text{conc. SO}_4^{=}} \right) = \frac{1}{74}; \text{ for } \frac{0.0006 \times 0.0006}{0.00007 \times 0.00007} = 74.$$

In case the concentration ratio is greater than $\frac{1}{74}$, solid SrSO_4 will be converted into solid SrCO_3 .

Before the war the consumption of strontium compounds in the United States was small, but it increased greatly by 1918; for strontium salts were employed not only in red fire in pyrotechnics and in railroad flares and fuses, but in night signals at the military front and at sea. Strontium salts are also used in medicine.

BARIUM. Ba = 137.37

547. Occurrence and Properties. — Barium owes its name to a Greek word meaning *heavy*, for certain of its compounds are remarkable for their high density or specific gravity. Barium occurs principally as the minerals **barite** (heavy spar), BaSO_4 , and **witherite**, BaCO_3 . The former mineral is more abundant. It often contains calcium or strontium sulfate, with which it is isomorphous. It is mined extensively in Missouri, Georgia, and Tennessee. Germany is known to have large deposits of barite, and England has fairly large deposits of this ore and workable deposits of witherite.

The preparation and properties of metallic barium are similar to those of calcium and strontium.

Pure barium distills when a mixture of barium oxide and either aluminium or silicon is heated to a high temperature in an exhausted vessel.

Volatile barium compounds impart a beautiful green color to the non-luminous gas flame. Its spectrum contains a conspicuous green line and a yellow line, as well as many other lines. The barium-ion, Ba^{++} , is colorless and highly poisonous.

548. Barium Compounds. — The compounds of barium are quite similar to those of the other alkaline earth metals. They are usually prepared from barite, which is first transposed into the sulfide or the carbonate; by treating either of these compounds with acids, other salts of the metal are obtained.

Witherite (BaCO_3) is much more difficult to decompose than is limestone. When the compound is heated, however, with carbon and rosin it yields barium oxide, BaO ; for the carbon dioxide is reduced to carbon monoxide, which prevents the reverse action.

Barium monoxide, BaO , is prepared by strongly heating the nitrate. When heated in air to low redness, it is gradually transformed into the **peroxide**, BaO_2 , which is used for the preparation of oxygen and in the manufacture of hydrogen peroxide. It forms the hydrate, $\text{BaO}_2 \cdot 10\text{H}_2\text{O}$.

Barium hydroxide, $\text{Ba}(\text{OH})_2$, is much more soluble in water, than are the hydroxides of calcium and strontium. The hydrate $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ is very common. Barium hydroxide is a strong base; its solution is used as an absorbent for carbon dioxide.

Barium chloride, BaCl_2 , can be prepared by the action of hydrochloric acid on the carbonate or the sulfide; it forms the hydrate $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$. The salt finds application in the purification of table salt, removing all traces of sodium and magnesium sulfates; it is a chemical from which many other barium compounds are prepared.

Barium nitrate, $\text{Ba}(\text{NO}_3)_2$, is produced by dissolving the carbonate or the sulfide in nitric acid. The salt is a powerful oxidizing agent and is used in the production of green fire or Bengal fire in pyrotechnics, in the manufacture of certain explosives, in green signal lights, and to give a driftwood blaze to log fires. "Green fire" may be produced by burning a mixture containing 3 parts of potassium chlorate, 3 of sulfur, and 8 of barium nitrate. (CARE! Do not rub this mixture in a mortar.)

Barium chlorate, $\text{Ba}(\text{ClO}_3)_2$, is also used in pyrotechnics and explosives.

Barium sulfate, BaSO_4 , is the most widely used of barium compounds. The native mineral barite (heavy spar) is characterized by its great density. Being a very insoluble compound, it is readily obtained as a precipitate by treating a solution of a barium salt with a soluble sulfate or with sulfuric acid. Precipitated barium sulfate is sold under the name of **permanent white**, or **blanc fixe**; it is an excellent pigment and finds extensive use as such. It is also employed in the manufacture of rubber goods, putty, oilcloth, linoleum, and white paper.

Barium sulfide, BaS , is similar to the sulfides of calcium and of strontium.

Lithopone is a pigment containing barium sulfate and zinc sulfide:



This is an example of two soluble compounds interacting to form two insoluble ones. When made into paint lithopone has great covering power, does not darken in the presence of hydrogen sulfide or sulfur, and is not poisonous. It is extensively used as a flat wall paint.

Barium carbonate, BaCO_3 , is used in the manufacture of brick to produce an even color and to prevent a white efflorescence on exposed surfaces. It is also used in the manufacture of optical glass, flat wall paints, rat poisons, for preparing other barium compounds, etc.

The manufacture of barium chemicals practically began in the United States in 1915, and during that year 8,823 tons were produced. In 1918, the quantity produced increased to 23,186 tons — nearly treble the quantity produced three years earlier. The amount of ground barite produced in 1918 was 55,086 tons, and the lithopone 62,403 tons. In 1926 the United States produced about 233,000 tons of crude barite and 160,000 tons of lithopone, the latter having a value of \$16,000,000.

549. Detection of the Alkaline Earth Metals. — It may be stated, in general, that a compound of an alkaline earth metal, when moistened with hydrochloric acid, colors the Bunsen flame, *calcium imparting an orange-red; strontium, a brilliant crimson; and barium, a green.* They also give characteristic spectra.

Their soluble salts are not precipitated by hydrogen sulfide, by ammonia, or by ammonium sulfide; but are thrown down by

ammonium carbonate as carbonates, which are readily soluble in acetic acid. On the addition of potassium chromate to the acetic acid solution, yellow barium chromate is precipitated, leaving calcium and strontium in solution. A solution of a barium salt yields a precipitate at once when treated with a saturated solution of calcium sulfate, whilst strontium sulfate is precipitated slowly on boiling, and calcium is not, of course, precipitated. A saturated solution of strontium sulfate will precipitate barium, but not calcium.

EXERCISES

1. Outline the physical and the chemical characteristics of the alkaline earth metals, illustrating as far as possible by means of equations. What can you say as to the solubilities in water of their oxides, hydroxides, sulfates, and carbonates?

2. Write chemical equations to show the following: (1) calcium + water; (2) strontium hydride + water; (3) calcium nitride + water; (4) barium nitrate + heat; (5) calcium carbide + water.

3. Outline a general method for preparing the alkaline earth metals. Why are they called the "alkaline earth" metals?

4. Suggest a method for transforming an alkaline earth oxide into the corresponding sulfide. The sulfide of the alkaline earth metals glow in the dark. Explain. These sulfides are almost insoluble in water, yet they cannot be precipitated by the action of hydrogen sulfide on solutions of salts of the metals. Explain.

5. Explain the formation of a temporarily hard water; also the formation of caves in limestone districts. Explain the use of limestone as a flux.

6. Describe and explain the manufacture of quicklime, discussing the chemical reaction involved from the standpoint of chemical equilibrium. State the properties of lime.

7. What is mortar? Explain why it "sets." What are cement and concrete, and how are they produced?

8. When calcium is burned in air and the product treated with water, ammonia is formed. Explain.

9. Outline the occurrence, properties, and uses of gypsum. What are alabaster and satin spar and for what are they used? What is plaster of Paris? How is it manufactured? Explain its uses.

10. Write the names and formulae of the phosphates of calcium. Tell how the primary and tertiary salts may be obtained and point out their uses.

11. Give the preparation and uses of calcium cyanamide. How may sodium cyanide be manufactured from it?

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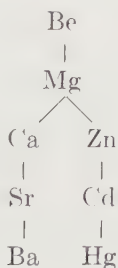
CHAPTER XXXI

THE MAGNESIUM GROUP

550. General Characteristics and Relationships. —

Element	Atomic Weight	Atomic Number	Density	Melting Point	Boiling Point
Beryllium, Be	9.02	4	1.84	1350°	1500°
Magnesium, Mg	24.32	12	1.74	651°	1120°
Zinc, Zn	65.38	30	7.14	419°	907°
Cadmium, Cd	112.41	48	8.64	321°	785°
Mercury, Hg	200.61	80	13.6	-38.8°	357°

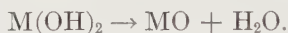
The Magnesium Family, like the family of the alkaline earths, falls in Group II of the Periodic System. The family contains *beryllium*, *magnesium*, *zinc*, *cadmium*, and *mercury*. The relationship of the two families is brought out in a general way by the accompanying diagram.



Beryllium and magnesium have a number of properties in common with calcium, strontium, and barium: *e.g.*, their oxides and hydroxides are more basic than are those of zinc, cadmium, and mercury. The hydroxide of beryllium is also feebly acidic: thus, it dissolves in cold alkali hydroxides, whilst magnesium hydroxide does not.

Beryllium and magnesium resemble zinc more than they do the alkaline earth metals, and may therefore be placed in Group II B. These two elements are sometimes regarded as linking the alkaline earth group to zinc, cadmium, and mercury.

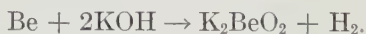
The general characteristics of the family are as follows: The elements are bivalent. Mercury is also univalent, forming two well-defined series of compounds (see Copper). The electropositive character of the metal decreases, as a rule, with increase in atomic weight, all being less electropositive than are the alkali metals. Mercury is by far the least active of the metals in the group, approaching the noble metals in its properties. Beryllium, however, lies between lithium and boron, so its hydroxide is amphoteric (see Zinc and Aluminium). Their sulfates are soluble in water (see CaSO_4 , SrSO_4 , and BaSO_4). Their hydroxides, when heated, readily lose the elements of water, forming oxides:



Unlike the alkali metals, they do not readily rust in the air. The metals have a silvery luster. They are much more easily obtained in the free state than are the alkaline earth elements. Their melting points and boiling points decrease with increase in atomic weight.

551. Beryllium, Be. — Beryllium was first prepared by Wöhler in 1828. Vauquelin, however, in 1798 detected its oxide in beryl. Beryllium is sometimes called **glucinum** (Greek, meaning *sweet*), because its salts possess a sweetish taste. Beryllium ores are fairly abundant both in this country and abroad. As compared with magnesium, however, the metal is not abundant. It occurs in many minerals, especially **beryl**, a metasilicate of beryllium and aluminium, $\text{Be}_3\text{Al}_2(\text{SiO}_3)_6$, or $3\text{BeO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$. The mineral beryl usually has a green color, probably due to traces of chromium silicate, but beryl of different colors occurs. **Emerald**, or precious beryl, is a transparent green. The best specimens of emerald come from the Republic of Columbia. At present beryllium ores are a waste material from New England feldspar mines.

Beryllium is prepared by the electrolysis of the double fluoride $\text{BeF}_2 \cdot 2\text{KF}$. Its melting point is $1,350^\circ$ and its density 1.84. When its powder is heated in air, it burns to form BeO . Its hydroxide is amphoteric. The metal displaces hydrogen from dilute acids; it also interacts with hot caustic potash:



Beryllium is about a third lighter than aluminium, but much harder. According to H. S. Cooper, it is over four times as elastic

as aluminium, and 25 per cent more elastic than steel. Unlike aluminium, it does not corrode readily when in contact with salt water. Beryllium forms some interesting alloys. An alloy containing 70 per cent of beryllium and 30 per cent of aluminium is one-fifth lighter than is aluminium; far more resistant to corrosion, and its tensile strength is far greater than that of duralumin. Moreover, beryllium expands under the influence of heat at about the same rate as does cast iron. It is possible, therefore, that there may be a considerable demand for the metal, especially in the construction of light alloys for airship frames, pistons, etc.

There are not many technical uses for beryllium compounds. The nitrate is added to the thorium solution employed for impregnating gas mantles; it appears to strengthen the ash skeleton of thoria (thorium oxide).

MAGNESIUM. $Mg = 24.32$

552. History and Occurrence. — This element derives its name from *Magnesia*, a town in Asia Minor. Davy isolated the metal in the impure state, in 1808. Bussy, in 1829, first obtained it as a coherent metal by fusing its chloride with potassium. Bunsen subsequently prepared magnesium by the electrolysis of its chloride.

Magnesium occurs in combination in great abundance and very widely distributed, constituting 2.24 per cent of the solid shell of the earth. Some of the most important minerals containing the metal are as follows:

Magnesite.....	$MgCO_3$
Dolomite (magnesian limestone).....	$MgCO_3 \cdot CaCO_3$
Talc, or soapstone.....	$H_2Mg_3(SiO_3)_4$
Meerschaum.....	$H_4Mg_2(SiO_3)_4$
Carnallite.....	$MgCl_2 \cdot KCl \cdot 6H_2O$
Kieserite.....	$MgSO_4 \cdot H_2O$
Epsom salt (Epsomite).....	$MgSO_4 \cdot 7H_2O$
Asbestos.....	$CaMg_3(SiO_3)_4$

All natural waters which have passed through magnesium-bearing rocks or minerals contain magnesium compounds. Normal sea-water contains about 0.5 per cent of magnesium chloride, the whole of the metal being reckoned as chloride. There is over 9 per cent in the Dead Sea.

Part of the calcium of calcium carbonate is sometimes displaced by magnesium, giving rise to dolomite. Talc is abundant in the Atlantic Coast States, and meerschaum is closely related to talc. Carnallite and kieserite are plentiful in the Stassfurt deposits. Asbestos is especially abundant in Canada.

553. Preparation. — *Magnesium is manufactured by the electrolysis of magnesium oxide dissolved in a bath of molten fluoride, principally magnesium fluoride.* The process is somewhat similar to the Hall process for producing aluminium (582). The anodes are carbon, which are oxidized to carbon dioxide by the liberated oxygen. The metal is set free at the cathodes, the oxide being added continuously.

The metal may also be produced by the electrolysis of either magnesium chloride or carnallite. A stream of hydrogen will protect the metal from oxidation. In 1918 the United States produced about 284,000 pounds of magnesium, and in 1926 the production was 390,400 pounds.

554. Properties. — Magnesium is a silvery white metal, with the density of 1.74; it melts at 651° and boils at about $1,100^{\circ}$. Just below its melting point it is ductile. When exposed to the air it becomes slowly coated with a basic carbonate, which protects the metal beneath. Magnesium is quite active chemically. When heated in air it burns brilliantly, forming magnesium oxide which contains some magnesium nitride. The light of burning magnesium is rich in waves of short lengths, which are useful in photography. Magnesium, when hot, combines with nitrogen to form the nitride (Mg_3N_2) and with chlorine to form the chloride. The metal readily displaces hydrogen from dilute acids, and interacts at high temperatures with water, yielding hydrogen and magnesium oxide. *Magnesium is a powerful reducing agent, for it has a high heat of formation:*



The heat of formation of carbon dioxide ($1/2 \text{CO}_2$) is only about 48,000 calories; therefore, magnesium will burn in CO_2 :



Magnesium for a similar reason will rob silicon dioxide, boron trioxide, and many oxides of metals of their oxygen. Magnesium cannot be deposited electrolytically from solution of its salts, for it has too negative a normal electrode potential (616).

555. **Uses.** — Magnesium has a number of uses. Before the war it was used chiefly in the manufacture of the alloy magnalium and for deoxidizing non-ferrous metals, such as copper and aluminium; in the powdered form it was mixed with potassium chlorate in preparing flash-light powder for use in photography; it was also used in pyrotechny. During the war there was a greatly increased demand for the metal; for it was used in star shells, flares, projectiles (tracer bullets), as a high explosive ingredient, and as an alloy with aluminium in the production of airplane and frame castings.

The alloys of magnesium possess lightness as well as strength. **Magnalium** is an alloy of aluminium and magnesium, containing from 1 to 15 per cent of the latter; it is lighter, stronger, and harder than aluminium, and more easily machined.

Alloys containing 95 per cent of magnesium (remainder Zn and Cu) have about the same strength in cast form as some of the common cast bronzes. "**Electron**" contains 95 per cent of magnesium, 4.5 per cent of zinc, and 0.5 per cent of copper. It is very light, strong, and can be machined. Magnesium alloyed with still smaller amounts of certain other elements can be rolled or forged. Magnesium gas engine pistons and connecting rods have been successfully employed. This is the lightest material available for such use (see Beryllium).

MAGNESIUM COMPOUNDS

556. **The Oxide and Hydroxide.** — **Magnesium oxide**, or **magnesia** (MgO), is an exceedingly light, white powder prepared by heating the carbonate (magnesite) or by burning magnesium. Magnesia melts at about $2,250^\circ$, so it is employed for lining crucibles and furnaces and in the manufacture of firebrick. Calcined magnesia is a poor conductor of heat, and for this reason is used on a large scale for insulating pipes and boilers. Magnesium oxide slowly interacts with water to form the sparingly soluble hydroxide $\text{Mg}(\text{OH})_2$, which has an alkaline reaction. Both oxide and hydroxide readily interact with acids to form salts. They are used as antidotes for poisoning by strong acids.

By treating the moist hydroxide with magnesium chloride, a *hydrated basic chloride*, $(\text{Mg}(\text{OH})_2)_x \cdot (\text{MgCl}_2)_y \cdot (\text{H}_2\text{O})_z$, is obtained; it is used as a plaster-finish in building.

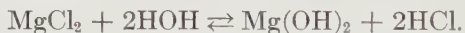
557. **Magnesium Sulfate, MgSO_4 .** — When magnesium sulfate crystallizes from cold water, the heptahydrate, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, is obtained in the form of rhombic prisms. This compound is commonly called *Epsom salt*, on account of its occurrence in the well-known mineral spring at Epsom, England (Dr. Grew, 1695). Many aperient mineral waters contain magnesium sulfate: for example, *Hunyadi water* contains Epsom salt, as well as sodium sulfate and sodium bicarbonate. Magnesium sulfate is used in coating cotton cloth, tanning, dyeing, the manufacture of soaps and paint, and in medicine.

558. **Carbonates of Magnesium.** — The **normal carbonate**, MgCO_3 , occurs abundantly as the mineral *magnesite*; it is used extensively in metallurgy as a lining for crucibles and furnaces, being consumed largely by steel plants and by manufacturers of refractory products.

The **basic carbonate**, $\text{Mg}(\text{OH})_2 \cdot 3\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$, known as *magnesia alba*, is produced by treating a solution of magnesium sulfate with sodium carbonate. (Why is the basic carbonate precipitated?) It is used on a large scale in the manufacture of cosmetics and tooth powders and for polishing silver.

Dolomite, $\text{MgCO}_3 \cdot \text{CaCO}_3$, is used extensively as a refractory and a building stone.

559. **Magnesium Chloride.** — The chloride, MgCl_2 , forms white deliquescent crystals, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$. When the hydrate is heated, partial hydrolysis occurs, hydrochloric acid being liberated:



When waters containing magnesium salts are used in boilers, the salts are more or less hydrolyzed, forming magnesium hydroxide, which deposits on the boiler tubes. The coating of **boiler scale** means that a larger amount of fuel is required to generate steam. It is difficult to remove the deposit, and now and then the thick scale cracks, which exposes the very hot iron to steam, giving rise to an explosion (why?).

560. **Other Magnesium Compounds.** — The **phosphate**, $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$, and the **pyrophosphate**, $\text{Mg}_2\text{P}_2\text{O}_7$, are of importance in analysis.

The **silicates**, such as talc, meerschaum, and asbestos, are very important. Talc is used in the manufacture of paper and toilet powder; soapstone or Albarene stone (a massive rock composed chiefly of talc) is quarried in large blocks and then manufactured

into various objects, such as laundry tubs, laboratory tables, hoods, tanks, pots, etc.; meerschaum is used for tobacco pipes, cigar holders, etc.; asbestos is used as cloth, felt, packing material, and for fireproofing in general. **Magnesium nitride** interacts with water to form ammonia:



561. **The Detection of Magnesium.** — Magnesium compounds possess very few characteristic properties which can be used in identifying the element. The magnesium-ion, Mg^{++} , is colorless, and the metal does not color the flame of a burner. We have seen that magnesium may be precipitated as the phosphate, $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$, which is a white crystalline salt, yielding the pyrophosphate at a high temperature. The metal may be precipitated as the hydroxide in case ammonium salts are not present. It cannot be precipitated, however, by ammonium hydroxide if ammonium salts are present also. This may be explained as follows: $\text{Mg}(\text{OH})_2$ is only slightly soluble in pure water, 100 g. of the solvent dissolving 0.001 g. of the base at 18° . The hydroxide ionizes thus:



but the product $[\text{Mg}^{++}] \times [\text{OH}^-]^2$ is low (see Solubility-Product, 254). When an ammonium salt, say, NH_4Cl , is present, the concentration of NH_4^+ represses the ionization of NH_4OH , lowering the concentration of OH^- so much that the product $[\text{Mg}^{++}] \times [\text{OH}^-]^2$ does not reach the value required for precipitation.

ZINC. $\text{Zn} = 65.38$

562. **History and Occurrence.** — Zinc (German, *zink*, probably akin to *zinn*, tin) did not come into general use until the nineteenth century. An idol containing 87.5 per cent of zinc was found in a prehistoric settlement of Transylvania. Two bracelets filled with zinc have been discovered in the ruins of Cameros, which was destroyed about 500 B.C. Brass, an alloy of zinc and copper, was known to the Romans, 200 B.C. Paracelsus, in the sixteenth century, showed that zinc is a metal. Zinc works were established at Bristol, England, in 1743. Zinc was first produced in the United States, in 1835–1836, by John Hitz in the arsenal of Washington, D. C.

Zinc occurs chiefly in the following minerals:

Zinc blende (German, <i>blenden</i> , to dazzle), sphalerite, or black jack	ZnS
Smithsonite	ZnCO ₃
Calamine	Zn ₂ SiO ₄ ·H ₂ O
Franklinite	Zn(FeO ₂) ₂
Zincite	ZnO
Willemite	Zn ₂ SiO ₄ .

The only known deposit of franklinite of importance is at Franklin and Stirling Hill, N. J. The ore occurs in limestone associated with zincite and willemite. New Jersey has one zinc mine which is said to produce 2,000 tons of ore daily.

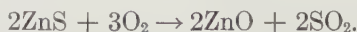
Zinc blende occurs abundantly in Missouri, Colorado, Kansas, Oklahoma, etc.

The world's production for 1913 was about 998,000 metric tons, of which the United States produced about 32 per cent, Germany 28, Belgium 20, France 6.5, Great Britain 6, and the rest of the world 7.5 per cent. In 1918 the United States produced more than 632,000 tons; while in 1924 the domestic production was 468,000 tons, the world's output amounting to nearly 1,000,000 metric tons. In 1926 the United States produced 612,000 tons, valued at \$92,000,000.

563. **Metallurgy.** — In case the ore is low-grade it is first concentrated, as in the oil flotation process. *In general, the ores of zinc are first converted into oxides by heating or roasting, and the oxide is then reduced with carbon (coal).* When smithsonite is heated, carbon dioxide is expelled:



The sulfide ore is roasted in furnaces, great quantities of SO₂ being obtained as a by-product:



Some zinc sulfate is formed when zinc blende is roasted, but at high temperatures ZnSO₄ loses SO₃, ZnO being formed.

The **Belgian process** is largely used for the reduction of the oxide. A mixture of the oxide and coal is placed in tube-shaped retorts (Fig. 173) of fire-clay, which vary from 3 feet 3 inches to 5 feet in length. A conical earthenware receiver terminating in an iron nozzle is luted to the open end of each retort, and 60 to 80 of the retorts are arranged in several tiers in a furnace and heated

by means of gas. At a high temperature (about $1,200^{\circ}$) the oxide undergoes reduction, the carbon monoxide burning at the nozzle:



As the temperature is above the boiling point of zinc (907°), the metal passes off as vapor and condenses for the most part in the receivers, whilst zinc dust and zinc oxide collect in the iron nozzles. The liquid zinc is removed from time to time and cast

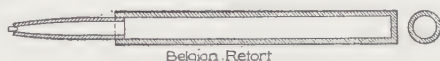


FIG. 173.

in blocks called **spelter**. The impure metal may be purified by distillation. The mineral zinc blende contains more or less of the sulfides of such metals as lead, cadmium, iron, arsenic, and gallium. Commercial zinc ordinarily contains traces of cadmium, iron, arsenic, sulfur, and carbon. *Cadmium has a lower boiling point (778°) than zinc*, so advantage of this fact is taken in separating these metals.

Zinc is also produced on an industrial scale by the electrolysis of solutions of zinc salts prepared from zinc ores. It may be that the electrolytic method will ultimately displace the smelting of zinc ores. Electrolysis is not only applied to mixed ores, such as copper-zinc and lead-zinc sulfides, but it is now applied to pure zinc ores. As a rule, a solution of zinc sulfate is prepared, which is then electrolyzed, an insoluble sheet-lead anode and a sheet-aluminium cathode being employed. When zinc blende is roasted, ZnO and ZnSO_4 are formed. By treating the roast with water and sulfuric acid, ZnO is changed to ZnSO_4 . When the electrolysis is carried out, the zinc-ion (Zn^{++}) is discharged on the cathode, which is melted and cast; sulfuric acid is formed at the anode and interacts with ZnO , forming more ZnSO_4 .

564. Properties of Zinc. — Zinc is a silvery white crystalline metal, which has a density of 7.10; it melts at 419° , boils at 907° , and at 120° – 150° it is malleable and ductile, but becomes brittle again at 200° – 300° . When melted and poured slowly into water, it forms granulated zinc. The vapor density of zinc at $1,740^{\circ}$ is 2.38 (air = 1), showing that its molecular weight is 68.9 (187). *The vapor is therefore monatomic.* Dry air or air free from carbon dioxide does not tarnish zinc at ordinary temperatures; but

moist air oxidizes the surface, a grayish coating of basic carbonate being formed. The approximate composition of the compound is $\text{ZnCO}_3 \cdot 3\text{Zn(OH)}_2$; it protects the metal from oxidation. At about 500° zinc burns with a bluish-white flame, forming finely divided zinc oxide. Zinc dust sometimes ignites spontaneously, and the dust suspended in air may explode. Commercial zinc interacts readily with dilute acids, forming hydrogen, but pure zinc dissolves very slowly (explain). Zinc interacts with the hot caustic alkalies, hydrogen being formed, as well as a zincate:



Zinc, as a rule, is electropositive to the heavy metals and thus precipitates them from solutions of their salts. Iron, manganese, and nickel are exceptions. Zinc can be deposited electrolytically: for instance, iron may be electrogalvanized by deposition of zinc from a solution of zinc sulfate and sulfuric acid.

565. **Uses.** — Zinc has almost innumerable uses. Sheet zinc serves for roofs, gutters, piping, bath tubs, wash-boards, etc. Zinc shavings are used as a precipitant of gold and silver from cyanide solution (485). Zinc is cast in the form of ornaments, statues, and blocks for hats. The metal is used to prepare zinc oxide (a white paint), in batteries, as a reducing agent, and for generating hydrogen. *Iron is galvanized by dipping the clean metal into a bath of fused zinc*, the latter metal furnishing a protective coat, which prevents rusting. By covering iron with zinc dust and then heating, **sherardized iron** is obtained. Vast quantities of zinc are used in the manufacture of alloys, such as brass, antifriction (white) metal, Babbitt metal, die-castings, and German or nickel silver. **Brass** contains from 18–40 per cent of zinc (see Copper). Certain antifriction metals contain from about 75–85 per cent of zinc, together with copper, and either antimony or tin. **German silver** is an alloy of zinc, nickel, and copper.

COMPOUNDS OF ZINC

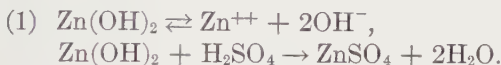
566. **The Oxide and Hydroxide.** — **Zinc oxide**, ZnO , is manufactured on a large scale by burning the vapor of the metal:



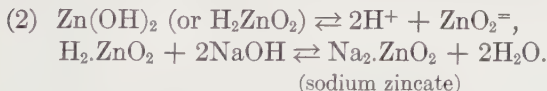
It also may be produced by calcining ZnCO_3 , Zn(OH)_2 or ZnSO_4 , or by roasting ZnS . The oxide is white while cold, but yellow

while hot; it is known as **zinc-white** or **Chinese white**, and is used in paint (not darkened by hydrogen sulfide) and as a filler in automobile tires; it is also used in the manufacture of oilcloth. With phosphoric acid it hardens, producing a dental cement.

Zinc hydroxide, $\text{Zn}(\text{OH})_2$, may be obtained as a white flocculent precipitate by treating a solution of a zinc salt with an alkali. The compound is almost insoluble in water, but is readily soluble in acids and in an excess of the alkalis. *The hydroxide is, therefore, amphoteric in character*; that is, it ionizes both as a base and as an acid:

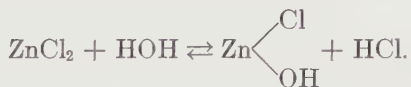


In this reaction the hydroxide functions as a base.



In this case zinc hydroxide behaves as an acid.

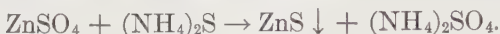
567. **Zinc Chloride**, ZnCl_2 . — Zinc chloride may be formed by conducting dry chlorine through molten zinc, through zinc oxide heated to redness, and by chloridizing the roast of zinc sulfide. Zinc chloride is very deliquescent. Since the chloride is a salt of a weakly basic metal, it tends to undergo partial hydrolysis:



It is used in the solid state as a caustic. Its solution is injected into wood, such as railway sleepers, as a poison to prevent decay. A hot solution of the salt dissolves cellulose.

568. **Zinc Sulfate**. — The sulfate ZnSO_4 is prepared on a commercial scale by roasting zinc sulfide. **Zinc sulfate** or **white vitriol**, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, is prepared by dissolving zinc or zinc oxide in sulfuric acid (see Epsom salt). It forms white orthorhombic crystals, and the solution has an astringent taste. Zinc sulfate is used in the printing and dyeing of cloth, and in medicine (*e.g.*, as an eye-wash). Like other soluble zinc compounds, it is poisonous.

569. **Other Zinc Compounds.** — Zinc sulfide, ZnS , occurs extensively as the mineral zinc blende. It may be prepared by treating a solution of a zinc salt with ammonium sulfide:



It also may be prepared by treating a solution of zinc acetate (salt of a weak acid) with hydrogen sulfide (write equation). (Why is the sulfide precipitated incompletely or not at all in the presence of an active acid?) Zinc sulfide is a white compound, which is used as a component of the pigment *lithopone* (548).

Zinc carbonate, ZnCO_3 , occurs as the mineral *smithsonite*. When a solution of a zinc salt is treated with an alkali carbonate, such as Na_2CO_3 , a basic carbonate is precipitated (why?). The composition of this carbonate depends upon conditions. The normal carbonate may be formed by employing sodium bicarbonate:



When ZnCO_3 is heated, it forms ZnO and CO_2 .

570. **Detection of Zinc.** — Zinc may be separated from the metals of the alkali and alkaline earth families by means of the reagent ammonium sulfide, $(\text{NH}_4)_2\text{S}$. The white precipitate zinc sulfide (ZnS) is soluble in active acids, but practically insoluble in acetic acid and in dilute alkalies. Zinc also is precipitated as the hydroxide by caustic alkalies, the precipitate being soluble in excess of alkali. When a zinc compound is heated on charcoal, the resulting oxide is white while cold, but yellow while hot; it turns green when treated with cobalt nitrate. Zinc-ion, Zn^{++} , is colorless and poisonous.

CADMIUM. $\text{Cd} = 112.41$

571. **Occurrence and Preparation.** — **Cadmium** (Greek, *cadmia*, calamine) was discovered in 1817 by Stromeyer in zinc ores. The metal occurs as sulfide (CdS) in the somewhat rare mineral *greenockite* (Greenock, Scotland). Cadmium is found associated with the ores of zinc, as much as 4 or 5 per cent being present in certain ores. *The cadmium of commerce is obtained from zinc minerals and ores.* In zinc smelting, cadmium, being more volatile than zinc, passes over first, with more or less zinc dust, as a brownish powder. The powder is distilled with a reducing agent,

yielding cadmium which still contains some zinc. By repeating the process the metal may be further purified. Cadmium and zinc are very closely related; hence the former constitutes a fraction of about 1 per cent of almost all spelter.

The cadmium industry began in the United States in 1907. In 1917, we produced over 207,000 pounds. From 1907 to 1913 Germany produced, on the average, about 84,000 pounds annually. In 1926 there were over 810,000 pounds of cadmium produced.

572. Properties and Uses. — Cadmium is a silver-white, fibrous metal, having very much the appearance of zinc. It melts at 321° , boils at 778° , and has a density of 8.64. The metal is harder than tin and is malleable and ductile. It interacts with dilute acids, yielding hydrogen, but is less reactive than is zinc. Cadmium is less easily oxidized than zinc. When heated in air, it burns to form the brown oxide, CdO .

Cadmium is used in the manufacture of **fusible alloys** (Wood's metal, etc.). During the war Germany was cut off almost entirely from the world's supply of tin, so cadmium was used in preparing solders. The metal appears to be a promising substitute for part of the tin in solders. The salts of cadmium are employed in the arts, in medicine, and in electroplating (better rust preventive than nickel). A small fraction of cadmium is also used in France and Italy as a deoxidizer in manufacturing bronze telegraph and telephone wires.

573. Compounds of Cadmium. — **Cadmium oxide**, CdO , is produced as a brown powder by oxidizing the metal. The **hydroxide**, $\text{Cd}(\text{OH})_2$, may be obtained as a white precipitate by treating a solution of a cadmium salt with a caustic alkali; it is not soluble in excess of the reagent, and is not amphoteric in character.

The **sulfide**, CdS , is produced as a yellow precipitate by treating a solution of a cadmium salt with hydrogen sulfide. The salt is practically insoluble in dilute hydrochloric or sulfuric acid. Commercially, it is the most important salt of cadmium, being known as "cadmium yellow," and is used as a pigment (street cars, passenger coaches, etc.). When properly prepared, it is one of the most permanent pigments known. The sulfide is used on a large scale to give color and luster to glass and porcelain. When a concentrated solution of cadmium sulfate is allowed to evaporate spontaneously, $\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ separates in monoclinic prisms. $\text{CdSO}_4 \cdot 7\text{H}_2\text{O}$ is also known, being isomorphous with $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$. Cadmium sulfate is used in diseases of the eye and in the con-

struction of cells of standard electromotive force ("normal cadmium cell"). Certain cadmium salts are used in photography and in dyeing.

The yellow color of the sulfide is of great importance in the detection of the element (arsenic and stannic tin must be absent). The metal also gives a brown incrustation when heated on charcoal. Cadmium-ion, Cd^{++} , is colorless. Cadmium sulfide is virtually insoluble in dilute hydrochloric acid, whilst zinc sulfide is soluble. Cadmium may therefore be separated from zinc by treating a hot, dilute hydrochloric acid solution of their salts with excess of hydrogen sulfide. Cadmium sulfide is insoluble in ammonium sulfide, whilst the sulfides of tin, arsenic, and antimony are soluble (645).

MERCURY. $\text{Hg} = 200.61$

574. Occurrence and Preparation. — **Mercury**, commonly called **quicksilver**, was known to the Greeks 300 B.C. The metal was named after Mercury, the messenger of the gods. It owes its symbol to the Latin word *hydrargyrum* (from Greek, meaning *water + silver*). The older alchemists were much interested in the examination of the properties of mercury.

Mercury occurs in small quantity in the native state. The source of the metal is the sulfide, or **cinnabar** (HgS). Mercury is produced chiefly in Spain, Italy, Austria, and the United States (largely California and Texas). The Almaden mine in Spain has been worked since about 400 B.C., and is still the greatest producer of mercury.

World's production of mercury in the years 1913 and 1917, in flasks of 75 pounds (1 metric ton = 29.395 flasks):

	1913	1917
United States.....	20,213	36,159
Austria.....	24,104	25,000
Italy.....	29,513	31,494
Spain.....	36,619	25,147
Other countries.....	6,606	7,000
Total.....	117,055	124,800

In 1926 the United States produced only 7,642 flasks, valued at \$702,000.

575. Metallurgy. — Mercury is obtained from cinnabar by heating the mineral either in furnaces or retorts, largely the former. When the ore is heated in furnaces, it is usually exposed

to the direct action of the flame, the metal being obtained by a combined roasting and distillation:



The volatile products, including the mercury vapor, are drawn into condensing chambers, and the mercury obtained as a liquid. When the ore is heated in closed retorts, lime may be added:



A temperature of about 360° is sufficient to decompose cinnabar and to volatilize the mercury. The metal may be purified by distillation *in vacuo*, or by treatment with dilute nitric acid. In the laboratory it is often freed from more active metals by allowing it to fall through nitric acid in the form of small globules.

576. Properties and Uses. — Mercury is a silver-white liquid with a density of about 13.6 at 0° ; it freezes at -38.8° and boils at 357° . Even at ordinary temperatures, mercury evaporates slowly. The vapor of mercury is colorless and consists of monatomic molecules (Hg). Both the vapor and the finely divided substance are poisonous. Thus, the use of retorts in the production of mercury is attended by the danger of *salivation*, or *mercurial poisoning*. Blue pills are prepared by triturating mercury with roots and honey. *When the vapor of mercury is heated well above its boiling point, it conducts electricity* (mercury lamps). Mercury forms amalgams quite readily with most of the other metals.

Chemically, mercury is not an active metal, approaching the "noble metals" in its properties. When heated in air to almost its boiling point, it becomes coated with mercuric oxide, which is unstable; it unites with sulfur and with chlorine, is insoluble in dilute hydrochloric and sulfuric acids, but interacts with nitric acid to form mercurous or mercuric nitrate, and with hot concentrated sulfuric acid to form mercuric sulfate and sulfur dioxide.

Mercury is used in the manufacture of drugs and chemicals (e.g., calomel, corrosive sublimate, and mercury fulminate); in electrical apparatus, mercury-vapor lamps, and storage batteries; in the amalgamation of gold and silver ores; in the manufacture of scientific instruments, thermostats, etc.; and as the cathode in certain electrolytic processes; also in dental amalgams.

The application of mercury vapor to power purposes was announced a few years ago. The metal is boiled and its vapor is utilized in driving a

turbine. The heat in the turbine exhaust is employed to generate steam. It appears that the mercury boiler is more efficient than is the usual steam distillation.

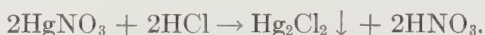
COMPOUNDS OF MERCURY

Mercury forms two well-defined series of compounds, namely, mercurous compounds and mercuric compounds. In the former the element is univalent (*e.g.*, Hg_2O , Hg_2Cl_2), and in the latter, bivalent (HgO , HgCl_2).

577. Mercurous Compounds. — **Mercurous chloride**, or **calomel**, Hg_2Cl_2 , the most important mercurous compound, is manufactured by heating mercuric chloride with mercury:



The salt is obtained as a white crystalline sublimate. It also may be prepared by the interaction of a solution of a mercurous salt and a soluble chloride:



The salt is practically insoluble in water, slowly affected by light (see Halides of Silver), mercuric chloride being formed, and is blackened by contact with ammonia, a mixture of Hg (black) and $\text{Hg}(\text{NH}_2)\text{Cl}$ being produced. The word "calomel" is derived from the Greek, meaning "beautiful black."

Calomel has long been used in medicine for the stimulation of secretory organs. It is best administered in very small doses with sodium bicarbonate to lower its solubility in the acidic gastric juice.

The **bromide**, Hg_2Br_2 (white), and the **iodide**, Hg_2I_2 (greenish-yellow) are also insoluble in water.

Mercurous nitrate, HgNO_3 , is prepared by treating an excess of mercury with dilute nitric acid of specific gravity 1.2. It is a monohydrate, $\text{HgNO}_3 \cdot \text{H}_2\text{O}$.

Mercurous oxide, Hg_2O , may be obtained as a brownish-black precipitate by treating a solution of a mercurous salt with sodium or potassium hydroxide.

As a rule, mercurous salts may be formed by the action of mercury on mercuric salts:



578. Mercuric Compounds. — **Mercuric oxide**, HgO , may be obtained as a red crystalline powder by heating mercury in the air or by calcining the nitrate; it also may be prepared as a yellow powder by the interaction of mercuric salts and caustic alkalies. It is an oxidizing agent, for it gives off oxygen when heated. Mercuric oxide is used in the preparation of paint for the bottoms of ships.

Mercuric sulfide, HgS , is the brilliant red pigment *vermilion*, which was known to the ancients. The salt may be prepared by heating a mixture of mercury and sulfur; it is used as a pigment, being more permanent in color than is red lead (Pb_3O_4). When a solution of a mercuric salt is treated with hydrogen sulfide, mercuric sulfide may be obtained as a black precipitate, which is insoluble in hot dilute acids, but soluble in *aqua regia*.

Mercuric chloride, or **corrosive sublimate**, HgCl_2 , is prepared by heating a mixture of mercuric sulfate and sodium chloride, a crystalline sublimate being formed:



Mercuric chloride is moderately soluble in cold water, but much more soluble in hot water. It is a violent poison, affecting the kidneys. It is coagulated by proteins; hence the white of egg is used as antidote for the poison. A solution of corrosive sublimate is a powerful antiseptic.

Mercuric iodide, HgI_2 , is obtained as a brilliant red precipitate by mixing solutions of a mercuric salt and potassium iodide, the precipitate being soluble in excess of either solution. When heated to 128° , it passes over into the yellow modification (117).

Mercuric nitrate, $\text{Hg}(\text{NO}_3)_2$, can be prepared by treating mercury with an excess of hot nitric acid of specific gravity 1.2. The salt is used in the manufacture of felt hats from rabbit's fur; for it roughens the hairs so that they will adhere together.

Mercuric cyanide, $\text{Hg}(\text{CN})_2$, is formed by treating mercuric oxide with hydrocyanic acid. When heated, it yields cyanogen gas:



An aqueous solution of the salt is but slightly ionized.

Mercuric fulminate, $\text{Hg}(\text{ONC})_2$, is prepared by treating mercury with strong nitric acid and alcohol. The salt is used as a detonator for high explosives, and to some extent in small-arms ammunition.

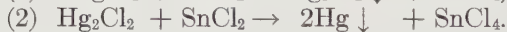
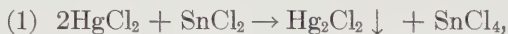
The discovery of mercuric fulminate led to the invention of the percussion cap, which displaced the old flintlock. The fulminate is still the most-used detonator for gunpowder and high explosives. It is often mixed with other substances, such as powdered glass, potassium chlorate, picric acid, trinitrotoluene, etc.

Mercuric thiocyanate, $\text{Hg}(\text{CNS})_2$, may be prepared by treating a solution of mercuric nitrate with one of potassium thiocyanate (KCNS). By kneading the dried salt with dextrin and water, forming it into little cones or pellets and then allowing them to dry, they will burn in air, leaving a voluminous ash ("Pharaoh's serpents").

579. Detection of Mercury. — In general, mercury compounds are completely volatile, with or without decomposition, when heated. By heating a small quantity of a mercury salt in a glass tube sealed at one end, a black sublimate may be obtained, which forms minute globules or turns red when rubbed. A strip of clean copper dipped into solutions of mercury salts displaces the mercury (explain from the ionic standpoint). A solution of a mercurous salt yields the white insoluble chloride Hg_2Cl_2 when treated with hydrochloric acid. The salt turns black when treated with ammonia:



When a solution of mercuric chloride is treated with a solution of stannous chloride, the reaction occurs in two distinct stages, — a white precipitate of Hg_2Cl_2 being first formed, followed by reduction of the calomel to mercury when the reagent is used in excess:



The mercury is obtained in the form of small gray globules. The ions of mercury, Hg^+ or $(\text{Hg})_2^{++}$ and Hg^{++} , are highly poisonous and colorless.

EXERCISES

1. Arrange the elements of Group II according to their atomic weights and so as to show the relation to each other of the two families constituting the group. State the general characteristics of the metals of the magnesium family.

2. Compare beryllium and magnesium, on the one hand, with the alkaline earth metals and on the other hand, with zinc.

3. Why is magnesium regarded as being more basigenic or electropositive than beryllium?

4. Outline the occurrence, preparation, properties, and uses of magnesium.
5. Explain as well as you can why magnesium may be burned in carbon dioxide, and why it will reduce such oxides as SiO_2 and B_2O_3 , as well as many of the oxides of metals.
6. Starting with dolomite show, including equations, how you would prepare MgO , $\text{Mg}(\text{OH})_2$, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{Mg}(\text{OH})_2 \cdot 3\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$, $(\text{NH}_4)\text{-MgPO}_4 \cdot 6\text{H}_2\text{O}$, and $\text{Mg}_2\text{P}_2\text{O}_7$.
7. Explain why zinc and cadmium may be precipitated electrolytically, whilst magnesium cannot be.
8. Explain: (1) Why sea-water cannot be used in boilers of ships; (2) why magnesium cannot be precipitated as hydroxide by ammonium hydroxide in the presence of plenty of ammonium salts; and (3) why magnesium cannot be precipitated as the normal carbonate.
9. Give the occurrence, metallurgy, properties and uses of zinc. What are the names and formulae of the important zinc ores found in the United States?
10. Starting with zinc blende, outline a method for the preparation of each of the following compounds: ZnO , $\text{Zn}(\text{OH})_2$, ZnCl_2 , $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, and ZnS (precipitated). What are the chief properties and uses of these substances? Explain fully, from the ionic standpoint, why zinc hydroxide is called an amphoteric substance.
11. Explain why pure zinc dissolves so slowly in dilute sulfuric or hydrochloric acid; also, why zinc dust and air may form an explosive mixture.
12. How would you separate zinc from calcium and magnesium and identify it? With what metal is zinc commonly associated in nature? How may they be separated?
13. Give the occurrence and sources of cadmium. How is it prepared? Why does spelter usually contain cadmium? What are the properties and uses of cadmium? State how you would prepare the most important cadmium salt, and point out its properties and uses. How would you prepare cadmium amalgam?
14. Explain from the standpoint of the ionic theory and equilibrium why cadmium as sulfide can be quantitatively precipitated by hydrogen sulfide in the presence of dilute sulfuric acid, while zinc cannot be precipitated thus.
15. Give the occurrence, metallurgy, properties, and uses of mercury.
16. What general methods would you employ (1) in the preparation of mercurous compounds and (2) mercuric compounds?
17. State how you would prepare the following compounds, giving their properties and uses: Hg_2Cl_2 , HgCl_2 , HgO , HgS , $\text{Hg}(\text{NO}_3)_2$, and $\text{Hg}(\text{OCN})_2$.
18. How would you detect mercury compounds, and differentiate between mercurous and mercuric compounds?
19. Show that mercury approaches the "noble metals" in its properties. Why, then, should it be classed with zinc and cadmium?
20. If you had a mixture of ZnS , CdS , and HgS , how would you separate and identify the metals contained therein?
21. In what respects does mercury resemble copper? Which is more positive? Explain. Which metal forms the more stable oxides? sulfates?

READINGS AND REFERENCES

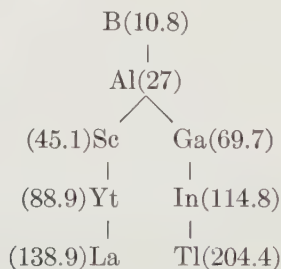
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CHAPTER XXXII

ALUMINIUM AND THE RARE EARTH METALS

580. **Relationships and General Characteristics.** — The elements occupying Group III of the Periodic System include two sub-groups or families: Sub-group III A includes scandium, yttrium, and lanthanum; and Sub-group III B, or the Aluminium Family, contains boron, aluminium, gallium, indium, and thallium. The relation of the families to each other is indicated by the accompanying diagram, the numbers in brackets being atomic weights. Boron and aluminium occupy a position in Group III similar to that of beryllium and magnesium in Group II. Since boron and aluminium are more closely related to gallium, indium, and thallium than to Sub-group A, they will be treated as members of Sub-group B.



Some of the characteristics of the elements of Group III are as follows: The elements are all trivalent, forming oxides of the type R_2O_3 . Thallium is also univalent (see the Alkali Metals and Silver). Boron is a non-metal, for its anhydride and hydroxide exhibit almost no basic properties. Boron also forms a hydride. Aluminium follows magnesium and precedes silicon in series, and possesses the physical properties of a metal. Chemically, it is more metallic than non-metallic, but its hydroxide is amphoteric in character; that is, it has both basic and acidic properties (see Zinc Hydroxide). Aluminium salts, such as its halides, are partially hydrolyzed by water. Aluminium is more electropositive than gallium; but indium and thallium are more electropositive

than their predecessors; that is to say, they follow the general rule, that the basic properties of elements increase with increase in atomic weight (see the Alkali Metals). The oxides of Sub-group A are more basic than are those of the Aluminium Family, for they do not form salts with strong alkalies.

Some of the physical properties of Sub-group III B are given in the following table:

Element	Atomic Weight	Atomic Number	Density	Melting Point	Boiling Point
Boron, B	10.82	5	2.34	2200°	3500°
Aluminium, Al	26.97	13	2.7	659°	1800°
Gallium, Ga	69.72	31	5.9	30°	1600°
Indium, In	114.8	49	7.4	155°	1450°
Thallium, Tl	204.39	81	11.8	302°	1650°

An examination of the table shows that the density increases with increase in atomic weight, while the melting point decreases abruptly from boron to gallium (this element would liquefy on a very hot summer day), and then increases to thallium. All these elements have odd atomic numbers.

Boron and aluminium are abundant, but the other elements of the family are rare and scarce. **Gallium** is of special interest owing to the prediction of its existence by Mendeléeff four years before its discovery. Lecoq de Boisbaudran discovered the metal in zinc blende by means of the spectroscope. **Indium** was discovered in zinc blende by Reich and Richter, in 1863, by means of the spectroscope. Its spectrum contains two indigo-blue lines; hence the name of the element. **Thallium** (Greek, meaning *green twig*) was discovered by Crookes in 1861 in seleniferous flue-dust from a sulfuric acid plant in the Harz. It was discovered by means of the spectroscope and owes its name to the bright green line in its spectrum.

There are many **rare earth metals**, including lanthanum, cerium, etc. The term earth is applied to certain metallic oxides which were formerly regarded as elementary substances: *e.g.*, La_2O_3 , Yb_2O_3 , etc.

The rare earth metals have atomic weights between barium (137.37) and tantalum (181.5). They are listed in the table on page 596, together with some of their characteristics.

Some writers include *scandium* (83) and *yttrium* among the rare earth metals.

THE RARE EARTH ELEMENTS

Name	Symbol	Atomic Number	Atomic Weight	Density	Melting Point
Lanthanum.....	La	57	138.9	6.16	826° C.
Cerium.....	Ce	58	140.25	6.90	640
Praseodymium.....	Pr	59	140.92	6.60	940
Neodymium.....	Nd	60	144.27	6.90	840
Illinium.....	Il	61
Samarium.....	Sa	62	150.43	7.7	>1300
Europium.....	Eu	63	152.0		
Gadolinium.....	Gd	64	157.26		
Terbium.....	Tb	65	159.2		
Dysprosium.....	Dy	66	162.52		
Holmium.....	Ho	67	163.5		
Erbium.....	Er	68	167.7		
Thulium.....	Tm	69	169.4		
Ytterbium.....	Yb	70	173.6		
Lutecium.....	Lu	71	175.0		

The **Cerium Group** includes lanthanum, cerium, praseodymium, neodymium, and samarium.

The minerals containing the rare earths occur chiefly in Scandinavia, the Urals, America, Brazil, India, and Australia. They are usually silicates. The most important of the silicate minerals is **gadolinite** (after *Gadolin*, a Russian chemist); it is a silicate of beryllium, iron, and the metals of the **Yttrium Group**, a term applied to the elements having atomic numbers from 63 to 71. Phosphates, tantalates, fluorides, etc., also occur. **Monazite** is the chief source of the Cerium Earths; it is a phosphate, (Ce, La, etc.) PO_4 , which also contains thoria and silica. Monazite sands of Brazil, India, and the United States contain from 2.3 to 28 per cent of thorium oxide (ThO_2), or thoria, and about 30 per cent of ceria. Interest in the rare earths was greater after 1884, the year in which Auer von Welsbach invented the incandescent gas mantle, which consists of thoria and ceria in the ratio of 99 to 1.

Owing to the extraordinary chemical similarity of the members of the rare earths and to the further fact that they are associated in nature, it is very difficult to separate them and to prepare them in the pure state. In certain cases many hundreds of fractional crystallizations have been carried out to obtain a pure compound.

The rare earth metals are trivalent. They are comparatively reactive, burning in the air to form basic oxides of the type M_2O_3 . Lanthanum oxide, like quicklime, hisses with water. They

form hydrides of the formula MH_2 or MH_3 , and nitrides of the type, MN .

The rare earth elements have been subjected to X-ray analysis (86), and atomic numbers have been assigned to them. The most recent addition to the group is an element of atomic number 61. Its X-ray spectral lines were recognized by B. S. Hopkins of the University of Illinois, in 1926. He named the element *illinium*, with the symbol *Il*.

ALUMINIUM. Al = 27

581. **History and Occurrence.** — Aluminium or aluminum (Lat. *alumen*, alum) was first prepared in the metallic state by Wöhler in 1827. Deville, in 1854, was the first to isolate the metal in fairly large amounts, and he determined many of its properties.

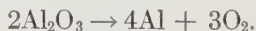
This metal is very abundant and widely distributed, constituting about 7.85 per cent of the solid shell of the earth, which places it first in quantity among the metals, and next to oxygen and silicon. It occurs in very great quantity as silicates, which make up the largest part of the earth's crust: *e.g.*, feldspar, clay, mica. Aluminium also occurs abundantly in Greenland as **cryolite**, Na_3AlF_6 (or $3NaF \cdot AlF_3$). The commercial source of the metal is the mineral **bauxite** (from the village of Baux, France), $Al_2O_3 \cdot 2H_2O$, which usually contains considerable quantities of hydrated ferric oxide. The quantity of bauxite marketed in the United States in 1918 was about 606,000 tons, most of which was produced in Arkansas. The mineral is also produced in Georgia, Alabama, and Tennessee. Valuable deposits occur in France, British and Dutch Guiana, India, Ireland, etc. As the high-grade bauxite is being rapidly consumed, it is important to perfect methods for the utilization of low-grade ore.

Aluminium also occurs as the oxide, Al_2O_3 , in the mineral **corundum**, of which the precious stones *ruby* and *sapphire* are varieties. The ruby owes its color to small quantities of chromium. When of the dark "pigeon blood" red of the right transparency, it is one of the most expensive of gems. The color of sapphire is due to titanium or iron. *Emery* is a compact or granular form of corundum containing a large proportion of oxides of iron. Corundum is exceedingly hard; hence it is employed as an abrasive. The weathering of feldspar gives rise to clay or kaolin. Alumina occurs in all fertile soils, but is found in small quantities only in most plants.

582. Preparation. — Formerly (Wöhler, 1827) aluminium was obtained by fusing together aluminium chloride and potassium in a closed crucible. In 1854 Bunsen obtained the metal by the electrolysis of the chloride. Shortly afterwards, Deville and other chemists prepared aluminium on a large scale by heating the double chloride of aluminium and sodium with metallic sodium and a flux. In 1855 the price of aluminium in France was \$115 per pound. By the year 1886 the American chemist Castner had succeeded in producing cheaper sodium, which forced down the price of the metal to \$4 per pound. In 1883, the total production was about 85 pounds.

In 1886 C. M. Hall, a student in Oberlin College, invented an electrolytic process for the manufacture of aluminium. The

Hall Process has been a great success, and the production of the metal has increased enormously and the price has been greatly cheapened. The process may be described briefly as follows: Alumina (Al_2O_3) is dissolved in a bath of molten cryolite and an electric current passed through the solution. The operation is conducted in cells lined with carbon, which constitute the cathodes. Carbon bars form the anodes, which combine with the oxygen (Fig. 174). Aluminium sinks to the bottom and is withdrawn from time to time. The electrolyte is decomposed thus:



In 1889 Hall organized a company for the commercial production of aluminium. By 1914 the annual domestic production of the metal was valued at more than ten million dollars, and the price had fallen to about 18 cents per pound. In 1918 the world's consumption of aluminium was about 500,000,000 pounds, owing to the abnormal demand for use in the war, of which the United States produced almost half. The value of the aluminium produced in the United States in 1926 was \$37,583,000.

The output of aluminium on the Western Hemisphere is controlled by the Aluminum Company of America, most of the metal being produced in the United States. The plant at Niagara Falls has a capacity of about 30,000 metric tons *per annum*.

As previously stated, bauxite is the source of aluminium. Most of the oxide occurring in nature has to be refined before use. In order to free the ore of iron oxide it is heated with concentrated

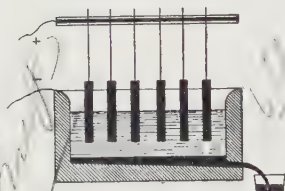
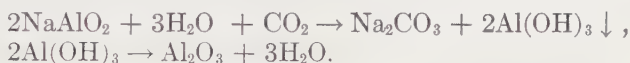


FIG. 174.

sodium hydroxide solution, or with dry sodium carbonate, the ferric oxide remaining unchanged and the alumina forming soluble sodium metaluminate (NaAlO_2). Aluminium hydroxide is precipitated by passing in carbon dioxide, and alumina obtained by heating the former:



583. Properties. — Aluminium is a silvery metal which resembles tin in appearance. It melts at 659° and boils at $1,800^\circ$. The density of the cast metal is about 2.58, and of the rolled metal, 2.69. Aluminium is the third most malleable and the sixth most ductile metal, being especially malleable and ductile between 100° – 150° . It is a good conductor of electricity, and in tensile strength, weight for weight, it is succeeded only by the best cast steel and aluminium bronze. The metal is difficult to work on a lathe or to polish, but when alloyed with magnesium it can be machined (see Magnalium). Copper or zinc produces the same effect as magnesium.

Aluminium tarnishes but slightly in air and is attacked but superficially by water, a film of oxide being formed in each case which prevents further action. It unites readily with many of the non-metals, such as the halogens, with sulfur, etc. Aluminium, at high temperatures, has great affinity for oxygen, or it is a powerful reducing agent; it therefore robs nearly all metallic oxides of oxygen. The heat of formation of aluminium is very high:

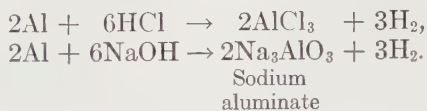


For the sake of comparison, *the heats of formation, per gram-atom of oxygen, of a few oxides are given below:*

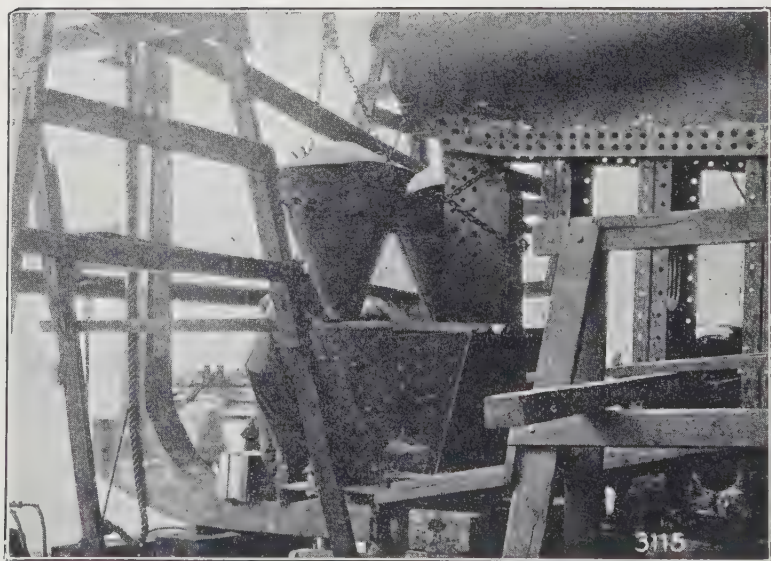
MgO.....	143,000 cal.
$\frac{1}{3} \text{Al}_2\text{O}_3$	128,700 "
Na_2O	100,900 "
$\frac{1}{3} \text{Fe}_2\text{O}_3$	65,200 "
$\frac{1}{2} \text{MnO}_2$	62,650 "

These heats of formation appear to explain, at least in part, why aluminium is so valuable in aluminothermy; in general, it will reduce metallic oxides having lower heats of formation than has Al_2O_3 . As MgO has a higher heat of formation, it cannot be reduced by aluminium. It is possible, however, that there are factors involved other than heat of formation.

Aluminium readily interacts with dilute hydrochloric acid and with hot solutions of alkalies to form hydrogen (compare with Zinc and Tin):



Clean aluminium vessels employed in the kitchen are but slightly attacked; the exceedingly small quantity of metal passing into the food would be very much less harmful to the human system



Courtesy, Metal and Thermit Corporation.

FIG. 175. Crucible in Position to Mend Sternpost of Boat.

than like quantities of copper. Aluminium forms an amalgam, which rapidly disintegrates on exposure to moist air, aluminium hydroxide being formed.

584. **Uses.** — Aluminium is a light, strong metal, and tarnishes but slightly, so it is used extensively in the manufacture of automobiles and airships. It also is used to free steel of air bubbles at the moment of casting it into ingots. Mixed with oil or other liquid, it is employed as a paint for metallic objects. It is further

used in the manufacture of cooking utensils, as a food wrapper, in the production of alloys, in aluminothermy (Fig. 175), and for long-distance power wires.

During the World War many new uses were found for aluminium: *e.g.*, one-third of the weight of the Liberty motor was composed of aluminium, and the finely divided metal was used in incendiary bombs, and as a component of certain explosives. New uses also were found for it in the construction of frames of airships and many parts of airplanes.

585. Alloys.—There are many alloys of aluminium. Its useful light alloys have densities which are usually from 2.8 to 3. Only a few of its alloys have been employed on a large scale. These include certain Al-Cu, Al-Zn, Al-Cu-Zn, Al-Si, Al-Cu-Si alloys, and duralumin and its related alloys.

Aluminium bronze contains 5–12 per cent of copper with aluminium. It has a splendid golden luster, is easily fusible, and has great chemical and mechanical resistance. An alloy containing 92 per cent of aluminium and 8 per cent of copper is used extensively for castings.

Duralumin or **duraluminium** means, in general, any light aluminium alloy susceptible of heat treatment, *i.e.*, hardening on quenching followed by aging. The composition of this class of alloys is variable. At the present time the ordinary duralumin is the most important. According to Anderson, simple duralumin in commercial use has a composition between the following limits:

	<i>Per cent</i>
Copper.....	3.5–4.5
Magnesium.....	0.5–1.0
Manganese.....	0.5–1.0
Aluminium.....	Remainder

The United States Bureau of Standards has discovered that duralumin can be protected against corrosion by coating with pure aluminium. Silicon is also present as an impurity, and it appears that it has a marked effect upon the hardening of the alloy, due to the action of the intermediate compound Mg_2Si .

In rolled, drawn and extruded shapes, pure aluminium is used where softness or high electrical conductivity is required. Aluminium alloyed with a little manganese is employed where a stiffer material is required, and duralumin where the greatest strength is required. The last obtains its greatest strength only after a

process of heat-treatment analogous to that of steel. The framework of the dirigible *Shenandoah* was constructed of duralumin.

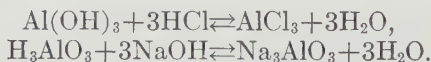
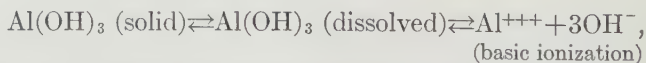
A variety of duralumin containing Cu 3 to 5 per cent, Mn 1 per cent, and Mg 0.5 per cent was extensively used in England during the War (Zeppelin airships); it has great tensile strength. Also a casting alloy (Al 88, Cu 12) was very popular in England (cylinders and pistons of aeroplane machines).

COMPOUNDS OF ALUMINIUM

586. The Oxide and Hydroxide.—Aluminium oxide or **alumina**, Al_2O_3 , is manufactured on a large scale from bauxite. We have already seen that it occurs in nature as corundum. Alumina obtained by heating the hydroxide is a white amorphous substance practically insoluble in water. It melts at about $1,900^\circ$, and crystallizes on cooling. Alumina is used to manufacture crucibles, tubes, etc. (*alundum*). Electrically fused alumina is an important abrasive. Without carborundum and alumina as abrasives for grinding it would be impracticable to produce automobiles or aircraft engines.

Artificial gems are now produced from molten alumina. The white sapphires are pure Al_2O_3 . It is changed into ruby by the addition of a trace of chromic oxide. Blue sapphires are obtained by adding traces of titanium oxide. The artificial sapphires and rubies are quite the equal of the natural gems. In the manufacture of gems, the pulverized oxides are melted in the oxyhydrogen flame and the droplets are caught on a disc in the flame and built up in the shape of an inverted chestnut. The oxide may be produced by sprinkling ammonium alum in the flame.

Aluminium hydroxide, $\text{Al}(\text{OH})_3$, may be obtained by treating a solution of an aluminium salt with ammonium hydroxide. The white gelatinous precipitate is insoluble in water; it is amphoteric in character, dissolving in acids to form salts and in the caustic alkalies to form aluminates:

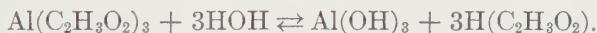


Sodium
aluminate

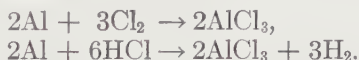
The *aluminates* are highly hydrolyzed by water, their solutions having an alkaline reaction.

Since aluminium hydroxide is a feeble base, such salts as Al_2S_3 and $\text{Al}_2(\text{CO}_3)_3$ cannot be formed in the "wet" way, *i.e.*, in the presence of water (explain in detail).

Aluminium hydroxide is used in the manufacture of alumina, as a mordant in dyeing, in the purification of water (see Aluminium Sulfate), in the manufacture of paper, etc. The hydroxide has great adsorptive power, probably being a colloidal gel. Aluminium hydroxide also is employed in **water-proofing cloth goods**. The cloth is steeped in a solution of aluminium acetate and is then steamed. The acetate is hydrolyzed, aluminium hydroxide being deposited in the capillaries of the cotton or linen, thus rendering the cloth impervious to water. The chemical change is shown thus.



587. Aluminium Chloride, AlCl_3 .— This important salt is manufactured by treating aluminium in a tube either with dry chlorine or hydrogen chloride (not quite dry), the chloride being obtained as a sublimate:



When $\text{Al}(\text{OH})_3$ is treated with hydrochloric acid and the solution concentrated, the hydrate $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ is obtained. (Why cannot the anhydrous salt be obtained by heating this hydrate?)

Aluminium chloride is a white crystalline salt, which fumes in the air, due to partial hydrolysis. It is used for the refining of mineral oils and as a catalyst in organic chemistry.

588. Aluminium Sulfate: The Alums.— Aluminium sulfate, $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, is prepared commercially by treating bauxite or kaolin with sulfuric acid, after roasting to render iron compounds insoluble. The aqueous solution of the salt is strongly acidic, on account of hydrolysis. This is the cheapest salt of aluminium; it is used on a large scale in the purification of water, in the manufacture of paper, and as a mordant in dyeing. In 1918 the United States produced about 209,000 tons of the salt.

The **alums** are double salts of the general formula $\text{M}_2^{\text{I}}\text{SO}_4 \cdot \text{M}_2^{\text{III}}(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$, in which M^{I} stands for an alkali metal (except Li) or the ammonium radical (NH_4) or silver, and M^{III} for a trivalent element (*e.g.*, Al, Cr, Fe^{III}). They are formed by mixing

solutions of salts of trivalent metals with those of the univalent metals and allowing crystallization to take place: *e.g.*, potash alum, $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$, can be prepared by dissolving potassium sulfate and aluminium sulfate in equi-molecular proportions and allowing the double salt to separate out. The transparent crystals are octahedral and belong to the regular or isometric system.

Some of the important alums are as follows:

Potash (common) alum.....	$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$
Sodium alum.....	$Na_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$
Ammonium alum.....	$(NH_4)_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$

The simpler formula $M^I M^{III} (SO_4)_2 \cdot 12H_2O$ is often used for the alums.

Alums are employed in the purification of water, in the manufacture of paper, and as mordants; they also are used in baking powders and in certain foods (*e.g.*, pickles). The United States produced in the year 1918 alums valued at more than \$1,000,000. Aluminium sulfate is displacing the alums; it is cheaper, but does not crystallize so well.

589. **The Spinel Minerals.** — *Magnesium metaluminate*, $Mg(AlO_2)_2$, occurs in nature as the mineral **spinel**. It crystallizes in regular octahedra, which may be colorless or variously tinted. Ruby spinel is very hard and is used as a gem. There are also other analogous and isomorphous minerals, constituting what is known collectively as the spinels. The following minerals will serve as illustrations:

Spinel.....	$Mg(AlO_2)_2$, or $MgO \cdot Al_2O_3$
Magnetite.....	$Fe(FeO_2)_2$, or $FeO \cdot Fe_2O_3$
Chromite.....	$Fe(CrO_2)_2$, or $FeO \cdot Cr_2O_3$
Franklinite.....	$Zn(FeO_2)_2$, or $ZnO \cdot Fe_2O_3$

590. **Aluminium Silicates.** — Igneous rocks make up a large part of the solid shell of the earth. These rocks contain on the average nearly 60 per cent of the **feldspars** $KAlSi_3O_8$ and $NaAlSi_3O_8$. The potash feldspars are called orthoclase and microcline, and the soda feldspar, albite. By the weathering of feldspars, which is partly chemical and partly mechanical, aluminium silicate, or clay, is formed (451); also, other components of the soil. The mineral **kaolinite**, $Al_2H_2(SiO_4)_2 \cdot H_2O$, is a pure variety of clay which is sometimes found deposited extensively in beds. More frequently, however, the kaolinite is carried away by running

water and deposited along with other substances such as sand and compounds of iron, calcium, and magnesium, forming what is known as common clay.

Kaolin is a pure form of clay, which burns white when heated, forming the basis of fine pottery and porcelain. The impure varieties of clay are utilized in the manufacture of tile, drain-pipes, bricks, etc.

591. **Ceramic Industries.** — The word pottery, in its widest meaning, includes all objects fashioned from clay and then hardened by means of fire or heat. Nowadays, **ceramics** (Greek, meaning *earthenware*) is the term generally employed for the study of the art of pottery. The ceramic industry therefore includes not only the production of pottery and porcelain, but brick, tile, etc. The arts of producing pottery, brick, and glass were practised by the primitive races of mankind.

The earliest pottery, which was produced by prehistoric man, was very crude. The clay was spread out on stones or slabs and kneaded by simple means to make it more pliable. Finally, it was fashioned by hand into the desired objects, and then dried in the sun. Pottery thus produced was soft and porous, as is the nest of the mud-wasp, but was suitable for containing dried grain, etc. In the course of many centuries fire was employed instead of the sun, which yielded pottery of various hues — buff, drab, brown, or red, due to the expulsion of water.

As previously stated, the purest variety of clay is kaolin, which is a salt, aluminium silicate, the formula for which may be written:



The melting point of pure clay is approximately that of platinum, 1755°C .

Kaolins are divided into two groups, the primary and the secondary kaolins. The primary clays have not been transported by water from the place where they were formed, while the secondary clays have been washed away from their original beds and deposited elsewhere. The latter variety has a much finer grain, is more plastic, though not so pure as the former.

Another variety of clay is called **ball clay**. The ball clays are secondary clays, are very plastic and strong, and when fired have a creamish or buff color. They impart strength to pottery. The purest form of clay is free from iron, so it fires to a pure white color, being used in the production of china and porcelain. Clay has the property of undergoing progressive hydration in contact

with water. Being very finely divided, it settles slowly when suspended in water, and in the solid state is very plastic. When the clay is heated, it loses water of hydration, forming a hard stone-like mass which has lost its plasticity. These properties of clay are the basis of the ceramic industry.

In preparation for molding (Fig. 176), the finely divided materials are mixed thoroughly with water, the suspension being known as **slip**. This is stored in large containers and pumped to the filter presses as needed, the object of the filtering operation



Courtesy of Ford Motor Co.

FIG. 176. Clay Pots for the Manufacture of Glass.

The clay is kneaded by the bare feet of the workmen. The pots are built by hand with infinite care, layer by layer, until all air-holes, fault lines, and incipient cracks have been eliminated.

being to squeeze out the water, leaving the clay in the form of cakes. Finally, the cakes are kneaded and worked up in a machine, the process being called **pugging**. The material is now ready for molding and shaping. This may be accomplished by three operations — jiggering, pressing, and casting. **Jiggering** is done by means of the mechanically driven potter's wheel, which is very ancient, its use being mentioned in the Old Testament. The mechanically driven wheel carries a plaster mold of the desired shape. The lower side of a piece of pottery is formed by revolving the mold, and the upper side by means of a steel profile, which can be raised and lowered.

A large dish may be made by throwing the clay upon a plaster mold, which shapes the inside. The outside is then finished by hand. This process is known as **pressing**.

All fabricated ware must be carefully dried in fire-clay recep-

tacles, called **saggers**. These are put into kilns and stacked up in tall columns. The temperature of the kiln, which may be heated by oil, usually varies from about $1,270^{\circ}$ to $1,400^{\circ}$, depending upon the object of the firing. Not only does the very high temperature of the kiln expel water, but other changes occur. The product of the first firing is porous and is called **bisque**. To render it impervious to liquids and gases, the porous ware is covered with a paste of finely divided feldspar and silica (or lead oxide or other suitable material) and fired a second time at a temperature high enough to melt the feldspar, which fills the pores. The articles may be decorated by means of suitable materials, such as the oxides of certain metals, followed by a third firing, which brings about the union and fusion of the oxides with the glaze. The colors are largely silicates. Cobalt oxide gives a blue glaze, chromium oxide yields green, etc.

Hard porcelain has a body consisting of kaolin, quartz, and feldspar. It softens only at the very highest temperatures, is harder than glass, and attacked by only a few chemical reagents, such as the caustic alkalies and hydrofluoric acid.

Porous ware is manufactured from plastic clays, and burned at a low or moderate temperature: *e.g.*, bricks, terra cotta, common crockery. Bricks and tiling are produced from common clay, and they owe their red color to ferric oxide (Fe_2O_3). Drain-pipes and bricks may be glazed by throwing common salt into the kilns (explain).

Fire-brick are manufactured from fire-clays, which are rich in silica and highly infusible, to which "grog" or silica is added. Refractory bricks for chemical furnaces contain magnesia, chromite, silica, etc., with enough plastic clay to make the material workable.

The **refractory industry** is one of the "key" industries. The employment of refractories for metal-melting furnaces and for the lining of furnaces is indispensable. The world's production of magnesite alone is over 500,000 tons per year, much of which is used for refractory purposes.

Zirconia, ZrO_2 , is even more refractory than silica; it is used in the manufacture of crucibles and as furnace linings for work at high temperatures.

592. Detection of Aluminium. — Ammonium hydroxide, as well as ammonium sulfide, precipitates aluminium as white gelatinous aluminium hydroxide, which is insoluble in the presence of ammonium salts. Sodium or potassium hydroxide produces the same

precipitate, which dissolves in excess of the reagent. When an aluminium compound is moistened with cobalt nitrate and then heated strongly, blue cobalt metaluminate, $\text{Co}(\text{AlO}_2)_2$, is formed. Aluminium hydroxide forms lakes with certain dyes, which are of use in its identification (737).

EXERCISES

1. Outline the relationships and general characteristics of the elements of the aluminium family. What is meant by the rare earth metals, and how are they related to aluminium?

2. What is monazite sand, where does it occur, and what very important substances are produced from it? Outline the manufacture of the Welsbach mantle.

3. Give the history, occurrence, preparation, properties, and uses of aluminium. Compare the preparation of aluminium with that of magnesium.

4. Give the composition of the following: alumina, ceria, thorium, bauxite, cryolite, corundum, ruby, spinel, calcium metaluminate, and potash alum.

5. Outline the preparation, properties, and uses of the following: (1) pure aluminium oxide from bauxite; (2) artificial rubies and sapphires; (3) aluminium chloride; (4) aluminium sulfate; (5) sodium alum. Define an alum, giving general chemical formula.

6. Explain the use of certain aluminium compounds in the purification of water, as mordants in dyeing, and in water-proofing cloth.

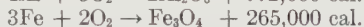
7. Show that aluminium hydroxide is amphoteric in character.

8. Why cannot AlCl_3 be prepared in the "wet" way? How is this salt prepared?

9. Zinc hydroxide dissolves in ammonium hydroxide, while aluminium hydroxide does not. Explain.

10. What is the tarnish on the surface of aluminium? Explain how this tarnish protects the metal from further oxidation.

11. From the following thermochemical equations show that aluminium will reduce magnetic oxide of iron (Fe_3O_4):



12. What volume of hydrogen, measured dry at 20° and 765 mm., could be obtained by treating 5.4 g. of pure aluminium with excess of sodium hydroxide?

13. The alums and the spinels are isomorphous compounds. Explain.

14. What very important minerals containing aluminium are found abundantly in igneous rocks? Explain how kaolinite is formed from feldspars. What is the difference between a primary and a secondary clay? Would you regard clay as being colloidal? Explain.

15. Outline the production of china and porcelain. What is the essential difference between porous and non-porous ware? How is pottery decorated? How are bricks and terra cotta produced? Explain why they may be red in color. What is the difference between ordinary brick and fire-brick? How would you render a clay more fusible? less fusible?

16. Explain the deportment of the following substances with water: B_2O_3 , Al_2O_3 , $AlCl_3$, (Al_2S_3) , and $Al(C_2H_3O_2)_3$. 6
17. Explain why aluminium is precipitated as $Al(OH)_3$ when a solution of an aluminium salt is treated with $BaCO_3$ suspended in water.

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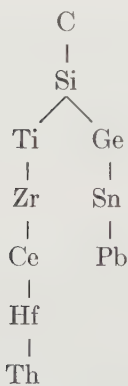
ROGERS. Elements of Industrial Chemistry. (Chap. VII deals with Ceramic materials and products.)

CHAPTER XXXIII

THE TIN GROUP

593. Relationships and General Characteristics. — The metals of the Tin Family are *germanium*, *tin* (*stannum*), and *lead* (*plumbum*). These fall in Group IV of the Periodic System, and are related to the non-metals, carbon and silicon, and to the weakly basic metals of the titanium-zirconium family, as shown by the accompanying diagram.

We may regard the elements of Group IV as a transition group, linking the more positive or basic elements of Groups I to III with the more negative or acid-forming elements of Groups V to VII. This means that metals predominate in Groups I to III, and non-metals in Groups V to VII; while in Group IV there is a sort of balance between metals and non-metals. In accordance with the general rule, the positive character of the metal increases with increase in atomic weight, lead being the most basic element of Sub-group B.



These elements possess a maximum valence of four, forming halides MX_4 , hydrides MH_4 , and oxides of the type MO_2 . Their dioxides are generally acidic in character. They also have a valence of two, cerium excepted, which may be trivalent. The elements of the titanium family also form oxides of the type MO_3 .

Tin and lead are not known to form hydrides, but they form *organo-metallic compounds*, such as lead tetraethyl, $\text{Pb}(\text{C}_2\text{H}_5)_4$. Moreover, the tetrahalides tend to unite with the corresponding halogen acids, as well as with the alkali salts, to form complex acids and salts, such as H_2SnCl_6 and $(\text{NH}_4)_2\text{SnCl}_6$.

The metals of the tin group are silvery white, easily fusible, and are not readily affected when exposed to the air. The metals of the titanium group are difficultly fusible.

The metals of the tin group unite directly with chlorine to form dichlorides and tetrachlorides — MCl_2 and MCl_4 .

The oxides and hydroxides of carbon and silicon are weakly acidic. The lower oxides of germanium, tin, and lead are basic and their higher oxides exhibit acidic properties. Titanium and zirconium are feebly acid-forming and base-forming, while cerium and thorium are base-forming.

Some of the properties of the members of the tin group are summarized in the table below.

MEMBERS OF THE TIN GROUP

Elements	Atomic Weight	Atomic Number	Density	Melting Point	Boiling Point	Oxides
Germanium, Ge	72.6	32	5.36	958°	2700°	GeO, GeO ₂
Tin, Sn.....	118.7	50	7.31	232°	2260°	SnO, SnO ₂
Lead, Pb.....	207.22	82	11.34	327°	1620°	PbO, PbO ₂

GERMANIUM. Ge = 72.6

594. **Germanium.** — This metal is of interest in that it was discovered by the German chemist Winkler in 1886, its existence having been predicted by Mendeléeff. It is a rare element. Winkler discovered it in a silver-bearing mineral found at Freiberg in 1885. The element was named **germanium** from the Latin word *Germania*. The metal may be prepared by reducing germanium dioxide, GeO₂, with carbon at a high temperature. Germanium melts at 958°, boils at 2,700°, and has a density of 5.36. It resembles silicon, but is more metallic in its physical properties. Like silicon, it is insoluble in hydrochloric acid, soluble in hot caustic alkalies, and burns in the air to form the dioxide. Like lead, it forms a tetraethyl compound, Ge(C₂H₅)₄. Its hydride, GeH₄, is unstable and volatile.

TIN (*Stannum*). Sn = 118.7

595. **History and Occurrence.** — Tin was one of the metals known to the ancients. Bronze (alloy of copper and tin) was very common in ancient times, and the metal itself was not uncommon. Tin has been discovered in Egyptian tombs. After Caesar's conquest of the British Islands, tin was carried from the Cornish mines to Italy. In olden times tin and lead were confused, but about the beginning of the Christian Era the Latin writer Pliny distinguished clearly between the two metals.

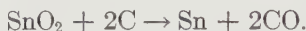
The chief ore of tin is the mineral **cassiterite** or **tinstone**, SnO_2 . The world's output of tin by smelting averages about 130,000 tons per year. It is produced largely by the Federated Malay States, Bolivia, and Banca. Considerable amounts of tin are also produced by China, Siam, Australia, and Cornwall. About 35 per cent of the world's production comes from the Malay States, 20 from Bolivia, and 10 from Banca. The rest of the world produces about 35 per cent—the amount produced by the Malay States. In 1916 the United States began to smelt imported tin-bearing concentrate, and in 1918 the amount of the metal produced was more than 10,000 tons. Some tin is recovered in this country from "tin cans."

596. **Metallurgy.** — The metallurgy of tin is very simple:

(1) The tinstone is crushed and the lighter earthy matter washed away.

(2) The ore is next roasted, if necessary, to remove arsenic and sulfur.

(3) The ore is then reduced with coal in a reverberatory or blast furnace:



(4) The metal is purified by remelting. When the cast slabs of tin are melted on the sloping hearth of a reverberatory furnace, the molten tin runs into a basin, while the iron remains behind.

A considerable quantity of tin is obtained by treating old "tin cans" and scrap tin-plate with chlorine. Stannic chloride, SnCl_4 , is formed, which is used in dyeing.

597. **Properties and Uses of Tin.** — Tin is a silvery white metal, melting at 232° and boiling at $2,260^\circ$; its density is 7.31, and it is a soft metal of no great tensile strength. When cold, it is rather brittle; and when a bar of the metal is bent, a peculiar crackling sound is emitted, known as the "tin cry." This is said to be caused by the rubbing of the crystals against one another. Tin is malleable at about 100° , and at that temperature it may be rolled into sheets (tin foil) and drawn into pipes.

There are two common modifications of tin, — **gray tin** and **white (tetragonal) tin** (Fig. 177). The metal is therefore *dimorphous*. The white modification is the common form of the metal. When white tin is exposed to low temperatures for some time, it slowly changes to a gray powder. Thus, in 1851, A. L. Erdmann observed that the tin pipes of an organ in a church at Zeita changed largely into a gray powder. During the winter of 1867–1868

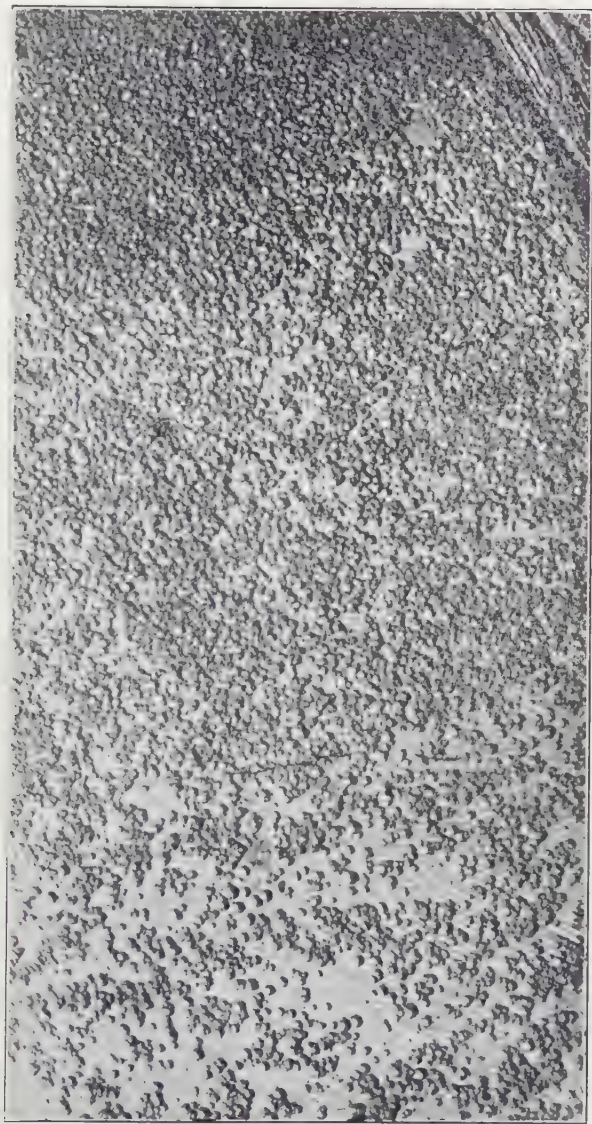


FIG. 177. The Tin Pest.

When white (ordinary) tin is exposed to low temperature, it slowly changes to the gray variety.

blocks of tin in St. Petersburg (Petrograd) underwent a similar change. This transformation of white tin into the gray form is called the "tin pest." The transition point is 13° . Above 13° , the white modification is stable, at 13° the two modifications are in equilibrium, and below 13° the change to the gray form occurs. The relation may be expressed thus:



This recalls the relation of rhombic to monoclinic sulfur (318)

Tin-plate is manufactured by dipping cleaned sheets of low-carbon steel into molten tin. The iron is thoroughly protected from corrosion so long as the coat of tin remains intact; but if the layer of tin be damaged, thus exposing the iron, corrosion of the latter is actually hastened, the tin serving as a contact agent. Ordinary *pins* are produced from brass wire and then coated with tin by treatment with a solution of a tin salt. Some of the zinc of the brass displaces tin, which coats the pins (explain in terms of ions and electrons).

Tin does not tarnish appreciably when exposed to moist air or to organic acids of food. The resistance of the metal to atmospheric corrosion and to the corrosion by organic acids is of the highest importance; for modern life is greatly dependent upon the "tin-can."

Tin dissolves slowly in dilute hydrochloric acid but rapidly in the concentrated acid, forming stannous chloride. Hot concentrated sulfuric acid converts it into *stannic* sulfate:



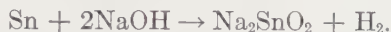
Dilute nitric acid slowly transforms it into stannous nitrate:



With concentrated nitric acid, stannic nitrate is first formed, but it rapidly hydrolyzes to β -metastannic acid.¹ When calcined in the air, stannic oxide (SnO_2) is obtained as a white insoluble powder. Tin combines directly with chlorine to form stannic

¹ The formula of this acid is somewhat variable. Under certain conditions it may have the empirical formula $\text{SnO} \cdot 2\text{H}_2\text{O}$; or it may be $\text{H}_2\text{Sn}_6\text{O}_{11} \cdot 9\text{H}_2\text{O}$, corresponding to $\text{K}_2\text{Sn}_6\text{O}_{11} \cdot 4\text{H}_2\text{O}$.

chloride, SnCl_4 . When heated with a strong solution of an alkali, tin forms a stannite and hydrogen:



Large quantities of tin are used in the production of tin-plate, from which cans, pails, cups, pans, tanks, etc., are produced. It also is used as a constituent of alloys, such as bronze, solder, bell- and speculum-metal, and Britannia metal. The addition of lead to tin lowers the melting point of tin, while the addition of tin to lead lowers the melting point of lead. **Common solder**,

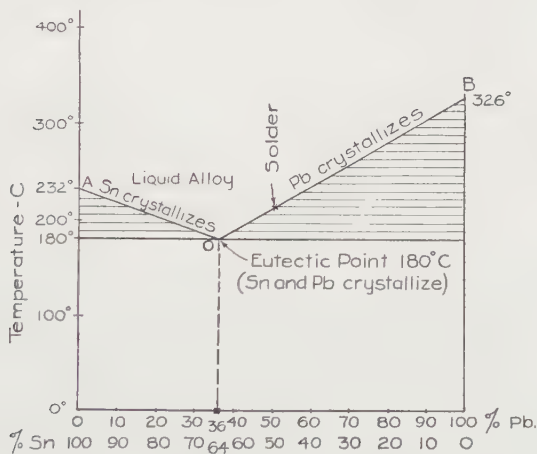


FIG. 178. Melting Points of Lead-Tin Alloys.

which readily melts, contains one part of tin to one part of lead. This solder begins to solidify at 220° . Plumber's solder contains one part of tin to two of lead, and it begins to solidify at 260° . An alloy containing 64 per cent of tin and 36 per cent of lead melts at 180° , the lowest possible melting point of an alloy of the two metals, as shown in Fig. 178. Tin and lead are completely miscible in the fused state, and form neither compounds nor solid solutions on solidifying. On the vertical axis of the diagram (Fig. 178) temperatures are indicated, while on the horizontal axis percentages of lead and of tin are shown. The curve AO is the **freezing point curve**, or **solubility curve**, of tin, and the curve BO is the corresponding one for lead. The two curves cut at O, which is known as the **eutectic point** (Greek, meaning *easily*

melted). The eutectic point is the point of maximum fusibility. Along the lines AO, BO the temperatures are shown at which an excess of one component freezes. At 180° the alloy freezes *en masse*; that is, the whole mass solidifies, the two metals crystallizing out side by side, forming a very intimate mixture.

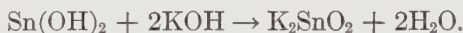
COMPOUNDS OF TIN

Tin, like mercury, forms two well-defined series of compounds — *stannous* and *stannic* compounds.

598. Stannous Compounds. — The **hydroxide**, $\text{Sn}(\text{OH})_2$, is a white substance obtained by treating a solution of stannous chloride with an alkali:

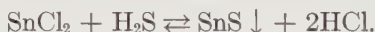


The precipitated hydroxide dissolves in an excess of the alkali, forming a **stannite**:

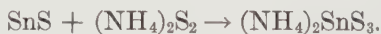


The hydroxide is amphoteric (566).

Stannous sulfide, SnS , may be obtained as a dark brown precipitate by treating a solution of a stannous salt with hydrogen sulfide:



The compound is practically insoluble in water and in dilute acids; it dissolves, however, in ammonium polysulfide, forming **ammonium thiostannate**:

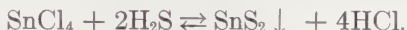


Stannous sulfide is soluble in concentrated hydrochloric acid; therefore this salt cannot be thrown down by hydrogen sulfide if the solution is strongly acid (see Arsenic).

Stannous chloride, or "**tin-salt**," $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, is used as a mordant in dyeing and as a reducing agent. A solution of stannous chloride has an acid reaction, due to hydrolysis.

599. Stannic Compounds. — **Stannic oxide**, SnO_2 , occurs in nature as the mineral cassiterite; it may be prepared by treating tin with strong nitric acid, evaporating to dryness, and igniting the residue; the white powder may also be obtained by heating tin in the air. It is insoluble in water and in acids (*i.e.*, when strongly ignited).

Stannic sulfide, SnS_2 , is obtained as a bright yellow precipitate by treating a solution of a stannic salt with hydrogen sulfide:



The salt is practically insoluble in water and in dilute acids; it is soluble, however, in strong hydrochloric acid and in the alkali sulfides:



The thiosalts are decomposed by acids:



The alkali sulfides, particularly the sulfides of ammonium, are used in analysis to separate the sulfides of tin, arsenic, and antimony from the sulfides of copper, mercury, bismuth, etc., the latter being insoluble.

Stannic sulfide, SnS_2 , in the form of "mosaic gold" is prepared by heating finely divided tin with sulfur and ammonium chloride. It is used as a pigment (*e.g.*, in gilding radiators).

Stannic chloride, SnCl_4 , is prepared by heating tin with excess of chlorine. It is a heavy, colorless, fuming liquid, boiling at 114° . In conjunction with small quantities of water it forms crystalline hydrates, such as $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ ("oxymuriate of tin"). When treated with more water, these hydrates dissolve; and *in dilute solution the salt is quite completely hydrolyzed*, the hydroxide forming a colloidal suspension:



Dilute solutions of stannic chloride have abnormally high conductivity for electricity and low freezing points, on account of the formation of hydrochloric acid by hydrolysis. In the case of dilute solutions the conductivity, at equilibrium, is identical with that of a solution of hydrochloric acid of equivalent strength, showing that hydrolysis is complete.

The hydrate $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ is used as a mordant.

Stannic chloride unites with hydrochloric acid to form **chlorostannic acid**, H_2SnCl_6 (or $2\text{HCl} \cdot \text{SnCl}_4$). Its ammonium salt, $(\text{NH}_4)_2\text{SnCl}_6$, is sold under the name of "pink salt"; it is used as a mordant in dyeing cotton goods.

α -Stannic acid, H_2SnO_3 , may be obtained as a white, gelatinous precipitate by the interaction of stannic chloride and ammonium hydroxide:



When heated it loses water, finally forming SnO_2 . **Sodium α -stannate**, $\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$, is used as a mordant and in fireproofing flannelette and other cotton goods (Sir William Perkin). The fabric is fireproofed by first soaking it in a solution of α -stannate; it is then dried, and treated with a solution of ammonium sulfate. The ammonium stannate formed undergoes hydrolysis, and the stannic acid which is formed cannot be washed out. When the fabrics are dried, the acid has a tendency to lose water to form stannic oxide.

When tin is oxidized with nitric acid, a hydrated stannic oxide is obtained, which is called **metastannic acid** or **β -stannic acid**. By boiling it with sodium hydroxide, sodium β -stannate, $\text{Na}_2\text{Sn}_5\text{O}_{11}$, is obtained. The acid is not identical with α -stannic acid. Thus, it is very slowly attacked by alkalis and is almost insoluble in dilute mineral acids, while α -stannic acid interacts readily with alkalis and with dilute mineral acids.

600. **Detection of Tin.** — The compounds of tin yield a metallic bead when heated on charcoal in the reducing flame. The metal is malleable and leaves a white insoluble residue when treated with nitric acid. Moreover, stannic salts yield a yellow sulfide when treated with hydrogen sulfide, while stannous salts give a brown sulfide. The ions Sn^{++} and Sn^{++++} are colorless.

LEAD. Pb = 207.2

601. **History and Occurrence.** — Lead was one of the seven metals known to the ancients. Articles manufactured of lead have been found in Egyptian tombs of great antiquity, and the metal is mentioned several times in the writings of the Old Testament. The ancient Romans utilized lead for water pipes, and certain lead compounds were used as paint and cosmetics. The Romans called it *plumbum*; hence the symbol Pb.

Lead occurs chiefly as the mineral **galena** or **galenite**, PbS , which crystallizes in the isometric system. Galena contains as impurities zinc, copper, cadmium, arsenic, antimony, and bismuth, perhaps as sulfides; also silver and gold. The silver value of a galena is often greater than that of the lead. Galena occurs

widely distributed, being found abundantly in the United States, Australia, and Spain.

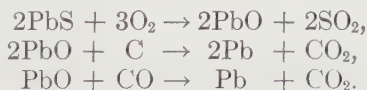
Cerussite, PbCO_3 ; **anglesite**, PbSO_4 ; and **crocoite**, PbCrO_4 , are also found. Next to galena, cerussite is the most important ore of lead; it is mined in Colorado, Arizona, and Utah. The mineral is formed as a secondary product in the superficial areas of lead deposits, being produced by the oxidation of galena and the action of carbonated waters.

The world's production of lead in 1913 was nearly 1,187,000 tons, of which the United States smelted about 34 per cent, Spain 17, Germany 15, Australia 10, Mexico 5 and Belgium over 4 per cent. The rest of the world smelted about 15 per cent of the metal. In 1917 the United States smelted about 512,000 tons, Spain 176,000, and Australia 145,000. The domestic production in 1926 was about 681,000 tons, valued at \$109,000,000.

The lead produced in the Mississippi Valley is mostly "soft lead," for the ores from which it is produced contain but little silver. "Desilverized lead" amounts to over two-thirds of our annual production.

In the United States, Missouri, Idaho, Utah, Colorado, and Oklahoma have produced the largest amounts of lead.

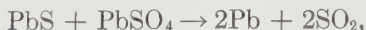
602. Metallurgy. — The smelting of lead ores can be carried out either in reverberatory furnaces or in blast furnaces, the greater part of the world's supply being produced in the latter. The ore or concentrate is first roasted in order to convert sulfide to oxide, and the product is then charged into blast furnaces with suitable fluxes and coke. A strong blast of air is passed through the charge, and the lead oxide is reduced, largely by the carbon and carbon monoxide:



The iron oxide formed is reduced by carbon monoxide to iron, which interacts with lead sulfide to form more lead:



Possibly lead sulfate (PbSO_4), formed by oxidation of PbS , interacts with the latter to form lead:



and PbO and PbS interact thus:



In case limestone is employed as a flux, lime combines with silica to form the fusible slag, calcium silicate.

The impure lead settles into the bottom of the crucible, whence it is drawn off into molds. The metal may be refined by slowly melting it down and stirring with a jet of steam. Impurities, such as iron, arsenic, antimony, and tin, are oxidized and are then skimmed off.

In case lead ores contain valuable quantities of the precious metals silver and gold, the metal is usually obtained by the Parkes process (see Silver).

Lead is also refined by an electrolytic process (see Copper Refining, 517). By the **Betts process**, an electrolytic bath containing lead fluosilicate, PbSiF_6 , is employed. Slabs of crude lead are employed as anodes and sheets of pure lead as cathodes. A little glue is introduced into the bath to render the deposit of metal more coherent. Impurities, such as copper, antimony, bismuth, and silver, are dropped as anode mud or are left undissolved as a skeleton of the anodes, while iron passes into solution.

603. Properties and Uses of Lead. — Lead is a silver-white metal, with a density of 11.4; it melts at 327° and boils at about $1,620^\circ$. The metal is soft and malleable, and while warm it may be fashioned into pipes by means of hydraulic pressure.

Chemically, lead is not very active, its position being below tin and above hydrogen in the electromotive series. Lead oxidizes only superficially in the air, a final covering of basic carbonate being formed, which protects the metal beneath.¹ When hard water remains in contact with lead pipes, a coating of the sulfate or the carbonate is formed, which protects the metal from further attack by the water. Soft water interacts with lead, however, to form the hydroxide, $\text{Pb}(\text{OH})_2$, which is appreciably soluble, and the lead-ion (Pb^{++}) is highly poisonous. When heated in air, it forms PbO or Pb_3O_4 , the latter being formed at lower temperatures. Most acids, excepting hydrochloric and sulfuric acids, interact with lead to form salts. Thus, it dissolves in nitric acid to form lead nitrate, and in acetic acid, forming lead acetate. Hydrochloric and sulfuric acids attack lead but slightly, for the chloride and sulfate are sparingly soluble.

¹ The writer recently examined a "cement" employed in the fifth century A.D. for fastening together pieces of bronze, and discovered that the surface of the binding material was lead carbonate, while underneath there was metallic lead. In the course of about 1,500 years, therefore, a considerable part of the lead had been transformed into carbonate.

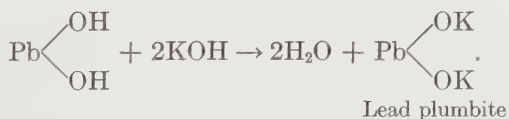
Lead has many industrial uses, among which are the manufacture of water-pipes, storage batteries, linings for the chambers of sulfuric acid plants, alloys (type metal, pewter, solder, anti-friction metal), paints, etc.

Antimony is one of the chief alloying elements used with lead. The lead of the storage battery is so alloyed; for without it the lead would be too soft. Lead for shot is hardened either with a little arsenic or antimony. The addition of the foreign metal renders the lead more fluid in the liquid state, increases the tendency to assume the spherical form, and makes the shot harder. **Shot** is manufactured by allowing the molten metal to fall from a tower, through openings in colanders, into water.

COMPOUNDS OF LEAD

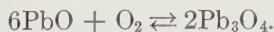
604. The Oxides and Hydroxides. — **Lead monoxide**, PbO , may be obtained as a yellowish-red, crystalline mass by the cupellation of lead (525). This form of the oxide is called **litharge**. A yellow, powdery form called **massicot** may be prepared by heating the carbonate or nitrate. All the other oxides of lead form PbO when heated in air at temperatures above 600° . Litharge is used extensively in the manufacture of flint-glass and as a glaze for pottery; also for preparing compounds of lead.

Lead hydroxide, $\text{Pb}(\text{OH})_2$, may be obtained as a white precipitate by treating a solution of a lead salt with an alkali; it is soluble in excess of sodium or potassium hydroxide, forming a *plumbite*:



$\text{Pb}(\text{OH})_2$ is slightly soluble in pure water, the solution being faintly alkaline.

Red lead, or **minium**, Pb_3O_4 , is prepared by the oxidation of massicot, PbO . The oxidation is carried out at a moderate temperature (not above 545°) in free contact with air:



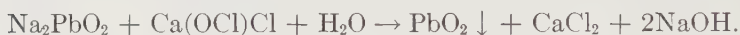
When red lead is treated with warm, dilute nitric acid, it undergoes decomposition, a brown powder of lead dioxide, PbO_2 , being

left as a residue. This indicates that red lead is **lead orthoplumbate**, Pb_2PbO_4 :



Pb_2PbO_4 may be regarded as a combination of the basic oxide, PbO , and the acidic oxide, $\text{PbO}_2(2\text{PbO} \cdot \text{PbO}_2)$. Minium is largely used as a paint and in the manufacture of flint-glass.

Lead dioxide, PbO_2 , may be obtained as already described, but is usually prepared by treating an alkaline solution of lead hydroxide with bleaching powder:



The precipitate is a chocolate-brown powder; it is a powerful oxidizing agent. Thus, it ignites a stream of hydrogen sulfide. When treated with concentrated hydrochloric acid, chlorine is liberated (271). This oxide may be regarded as the anhydride of orthoplumbic acid, $\text{Pb}(\text{OH})_4$, or H_4PbO_4 (see above). Orthoplumbates having the composition M_4^1PbO_4 are known.

Lead suboxide, Pb_2O , may be obtained as a dark-gray powder by carefully heating lead oxalate; it also forms as a thin coating on the surface of exposed lead.

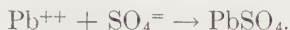
Lead sesquioxide or **lead trioxide**, Pb_2O_3 , is formed as a reddish-yellow powder by treating an alkali plumbite with a solution of sodium hypochlorite.

605. **Chlorides of Lead.** — **Lead chloride**, PbCl_2 , may be obtained as a white, crystalline precipitate by treating a solution of a lead salt with hydrochloric acid or a soluble chloride. It is sparingly soluble in cold water, but moderately soluble in hot water.

Lead tetrachloride, PbCl_4 , may be obtained by passing chlorine into the dichloride suspended in hydrochloric acid or by dissolving PbO_2 in well-cooled hydrochloric acid. It is a yellow fuming liquid (solid at -15°) which readily decomposes into the dichloride and chlorine.

606. **Lead Nitrate**, $\text{Pb}(\text{NO}_3)_2$. — This salt may be prepared by dissolving lead, lead monoxide, or lead carbonate in nitric acid. It crystallizes in white, anhydrous octahedra, and is very soluble in water. When heated, it yields oxygen, nitrogen peroxide, and lead monoxide (399). It is very commonly used in the laboratory.

607. Lead Sulfate, PbSO_4 . — This is a white salt which is almost insoluble in water. It is readily prepared by adding sulfuric acid to a solution of a lead salt:



It dissolves in a concentrated solution of sodium or potassium hydroxide and in ammonium tartrate. The salt is somewhat soluble in hot moderately concentrated hydrochloric acid and in nitric acid, as well as in hot concentrated sulfuric acid, from which solution it separates upon diluting with water.

"Sublimed white lead" consists of 75 per cent of lead sulfate, 20 of lead oxide, and 5 of zinc oxide; it is one of the lead pigments smelted directly from ore.

608. Lead Carbonate, PbCO_3 . — **Normal lead carbonate, PbCO_3 ,** occurs in nature as cerussite; it may be prepared by adding sodium bicarbonate to a solution of lead nitrate. When a normal alkali carbonate, such as Na_2CO_3 , is added to a solution of a lead salt, however, **basic lead carbonate, $\text{Pb}(\text{OH})_2 \cdot 2\text{PbCO}_3$,** is obtained (explain). This salt is identical with white

lead. The finest grade of **white lead** is manufactured by the **Dutch process** which has been in use for over 300 years. This process consists in exposing perforated sheets of lead ("buckles" (Fig. 179)) to the action of acetic acid vapor, moisture, and carbon dioxide. Small earthenware pots, each containing a shelf or ledge, are practically filled with dilute acetic acid (3–5 per cent of $\text{C}_2\text{H}_4\text{O}_2$), and on each shelf or ledge the perforated plates of lead are supported. The pots so charged are placed side by side upon a layer of moist spent tanbark which is ready to ferment. A board floor is supported a few inches above the pots, and upon this another layer of tanbark is spread. Other alternate layers of pots and tanbark are built up until a shed or room is almost full, the doorway being boarded up as the filling continues. The heat liberated by the fermentation of the tanbark vaporizes acetic acid and water, which interact with lead, forming a basic lead acetate. The carbon dioxide formed by fermentation transforms the acetate into basic lead carbonate, or white lead. The vapor of acetic acid may be regarded as a catalyst, for it is regenerated and used over again. The action is slow, about three months being required for the process to complete itself. Owing to the great



Courtesy, National Lead Co.

FIG. 179. A Lead Buckle.

length of time consumed in producing white lead by the Dutch process, it is not economical. Various rapid methods have been devised for the production of white lead, but the product apparently is not so satisfactory. The world's production of white lead is estimated to be 275,000 tons annually, about two-thirds of which is manufactured by the Dutch process.

White lead is ground with linseed oil and used very extensively as a paint; it has greater covering power than has zinc-white (566) or permanent white (548), but turns dark on exposure to hydrogen sulfide. The *body of a paint* is a solid substance, such as white lead, to which an oil is added. To hasten the drying of paint, a so-called "drying" oil, such as linseed oil, is employed, and is termed the *vehicle*. The oil undergoes oxidation, forming a hard mass. The process of oxidation may be hastened by boiling some of the oil with certain accelerators: *e.g.*, manganese dioxide. A cement composed of minium and linseed oil is used by plumbers for making joints tight. The oil is oxidized by the minium. In case a colored paint is desired, a pigment is added, such as red lead or chrome yellow. Painters sometimes have a violent form of intestinal colic known as "lead colic"; it is produced by chronic lead poisoning.

609. Other Compounds of Lead. — **Lead sulfide**, PbS , is obtained as a black precipitate by treating a solution of a lead salt with hydrogen sulfide. The salt is practically insoluble in water and in dilute acids, but soluble in strong, hot nitric acid:



The compound occurs abundantly in nature as galena.

Lead acetate or **sugar of lead**, $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$, may be readily prepared by dissolving PbO in strong acetic acid. The salt crystallizes in white monoclinic crystals having the formula $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$. It is one of the most soluble of lead salts, and the solution has a sweet taste; hence the name sugar of lead.

Lead chromate, PbCrO_4 , is readily prepared by treating a solution of a lead salt with a soluble chromate:



The salt has a fine yellow color, being known as *chrome yellow*. It is insoluble in water, but soluble in nitric acid. It is used as a pigment.

Lead arsenate, $\text{Pb}_3(\text{AsO}_4)_2$, may be prepared by treating a solution of a lead salt with sodium arsenate. The white salt is very

sparingly soluble in water. It is extensively used as an insecticide (629).

Tetraethyl lead, $\text{Pb}(\text{C}_2\text{H}_5)_4$, is employed as an "antiknock" in gasoline. The compound is unstable, tending to break down into lead and the very reactive ethyl group (C_2H_5).

610. **Detection of Lead.** — Lead can be easily detected, for it is precipitated as PbS (black), PbSO_4 (white), PbCl_2 (white and soluble in hot water), and PbCrO_4 (yellow). When a lead compound is heated on charcoal in a reducing flame, a bright malleable button of the metal is obtained. PbS is insoluble in ammonium polysulfide, which affords a means of separating lead from tin (630 and 645). The lead ion, Pb^{++} , is colorless and highly poisonous.

611. **The Storage Battery.** — In the construction of a **storage cell**, or **lead accumulator**, plates of leaden gratings are prepared, and one of the plates is filled with spongy lead and the other with lead dioxide, PbO_2 (see Fig. 180). Pairs of these plates are

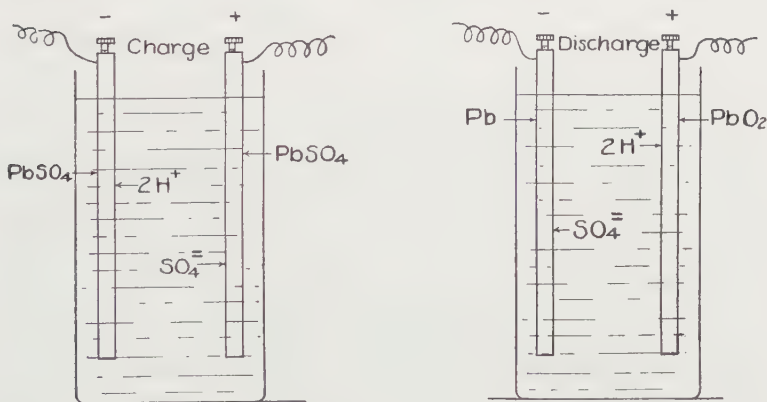


FIG. 180.

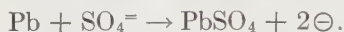
placed in a cell and dilute sulfuric acid (sp. gr. about 1.2) added. When the plates are connected by means of a wire, a current with an electromotive force of about 2 volts is produced as the cell is discharged. The chemical changes are as follows:

- (1) The hydrogen-ion reduces PbO_2 , forming PbO :



The plate acquires a positive charge, and the PbO interacts with H_2SO_4 to form PbSO_4 .

(2) The sulfate-ion interacts with the spongy lead forming PbSO_4 , the plate at the same time becoming negatively charged:

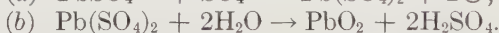
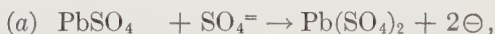


In these changes sulfuric acid is used up, so its density decreases as the battery runs down, *i.e.*, as its energy is consumed.

The exhausted storage battery is charged by passing through it a current from a dynamo. This current is passed in the opposite direction to that produced by the battery. The positive pole of the battery is connected with the positive terminal of the dynamo circuit, and the negative pole with the negative terminal (Fig. 180).

The chemical changes are as follows:

(1) The sulfate-ion is attracted to the positive plate where it interacts with PbSO_4 to form lead persulfate, $\text{Pb}(\text{SO}_4)_2$, which is hydrolyzed to PbO_2 and H_2SO_4 :



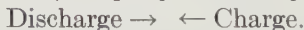
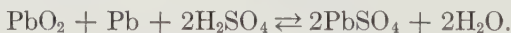
H_2SO_4 is therefore regenerated and the filling of the plate is changed into PbO_2 .

(2) The hydrogen-ion is attracted to the negatively charged plate, where it reduces PbSO_4 to Pb:



The battery has thus consumed energy, and it may be discharged again by connecting the wires of the plates.

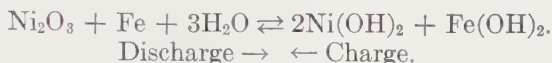
The chemical changes occurring both on discharge and charge may therefore be represented by the following reversible equation:



The lead storage battery was invented in 1860 by Gaston Planté.

In the **Edison storage cell**, the active material of the positive plate is an oxide or oxides of nickel, while that of the negative pole is iron. The electrolyte is 21 per cent solution of potassium hydroxide with a small amount of lithium hydroxide. When the cell discharges and is recharged the reversible action may be

shown by the following equation:



(What is reduced and what is oxidized?)

612. Sub-group IV A. —

Element	Atomic Weight	Atomic Number	Density	M.P.	B.P.	Typical Oxide
Titanium, Ti..	47.9	22	4.5	1800°	3000°	TiO ₂
Zirconium, Zr..	91.22	40	6.4	1700°	2900°	ZrO ₂
Cerium, Ce....	140.25	58	6.9	640°	1400°	CeO ₂
Hafnium, Hf...	178.6	72				
Thorium, Th..	232.15	90	11.2	1845°	3000°	ThO ₂

The elements of Sub-group IV A increase in metallic properties with increase in atomic weight. Titanium and zirconium are feebly base-forming, as well as acid-forming, while cerium and thorium are exclusively base-forming. They are elements of minor importance.

Titanium occurs principally in the minerals *rutile*, TiO₂, and *ferrous titanate*, FeTiO₃. Titanium constitutes nearly 0.5 per cent of the earth's crust. An alloy of iron and titanium is used as a deoxidizer in the production of steel. The alloy may be produced by the reduction of iron-titanium ore with carbon in an electric furnace.

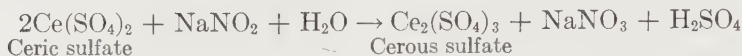
Zirconium occurs in zircon, which is a silicate of the metal (ZrSiO₄). *Zirconia* (ZrO₂) is employed as a refractory (crucibles, furnace linings, etc.); it melts, when pure, at about 3,000°.

Hafnium is very similar to zirconium. This element was discovered in 1923 by Costa and Hevesy, of Copenhagen (Lat. *Hafniae*).

Cerium and **thorium** and their compounds are obtained principally from monazite sands, chiefly along the coast of Brazil. When an alloy containing 70 per cent of cerium and 30 per cent of iron is struck by a file, particles are torn off which ignite in the air. This is the basis of certain gas-lighters and cigar-lighters.

Cerium forms two classes of salts, namely, *cerous* and *ceric*. The trivalent cerous salts are colorless compounds and may be regarded as derivatives of *cerous oxide*, Ce₂O₃. The ceric salts may be prepared from the dioxide, CeO₂. *Ceric sulfate is an oxi-*

dizing agent. Thus, it oxidizes nitrites and many other substances quantitatively:



Cerium also forms a *peroxide*, CeO_3 .

Thorium nitrate, $\text{Th}(\text{NO}_3)_4 \cdot 6\text{H}_2\text{O}$, is employed in the production of Welsbach mantles. *Thorium and its compounds are radioactive.* **Mesothorium** is used as a substitute for the more expensive radium, but it has a much shorter life.

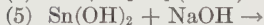
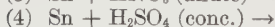
EXERCISES

1. In what group of the Periodic System do tin and lead fall? Show their relation to the other members of the group. Enumerate the general characteristics of the elements of this group.

2. Give the occurrence, metallurgy, properties, and uses of tin. What is the relation of gray tin to white tin? Can you mention other metals which illustrate the same relationship?

3. How can steel and brass be tinned? How can tin-plate be "detinned"? Why does defective tin-plate rust faster than iron?

4. Complete the following equations:



5. Explain, writing equations, how you would prepare the following compounds, and mention two properties and any uses of each: (1) $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, (2) $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, (3) SnS_2 , (4) $(\text{NH}_4)_2\text{SnS}_3$, (5) $\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$.

6. What is meant by the eutectic point of an alloy? Illustrate with solder. If a fused solder containing 60 per cent of lead were cooled, what would one observe?

7. Describe and explain the Perkin process for fireproofing flannelette.

8. How may a stannous salt be differentiated from a stannic salt? How would you separate tin from lead and identify the former? Cite evidence to show that tin is a weakly basic metal.

9. Outline the occurrence, metallurgy, properties, and uses of lead. What is meant by "soft lead," and where is it produced? What is meant by "desilverized lead"?

10. Explain the action of soft and of hard waters upon lead pipes.

11. Give the names and formulae of the oxides of lead. State which of these are the most important, explain (with equations) how they may be prepared, and mention their chief uses. Show that $\text{Pb}(\text{OH})_2$ is amphoteric, and that Pb_3O_4 is probably lead orthoplumbate.

12. Formulate the action of potassium hydroxide and of acetic acid upon lead hydroxide. What evidence can you cite to show that lead is more electropositive than tin?

13. Describe the Dutch process for the manufacture of white lead. How is it treated for use as a paint? What are the advantages or disadvantages of this paint as compared with zinc-white and permanent white? It is a good plan for workers in white-lead plants to add a very small quantity of sulfuric acid to their drinking water. Explain.

14. Why cannot concentrated sulfuric acid be kept in lead-lined containers? Why can it be kept in containers of certain iron alloys?

15. How can lead be detected? How would you differentiate beads of silver, tin, and lead? How would you test a sample of water for lead? If you suspected that an animal had been poisoned by eating "red lead," how would you test for the substance?

16. Explain the chemistry of the lead storage cell.

17. Mention some uses for titanium, zirconia, thoria, and mesothorium.

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CHAPTER XXXIV

ELECTROCHEMISTRY

613. **Electrical Energy and Electrical Units.** — Electrical energy can be produced by chemical change, the source of the energy being the chemical energy stored in the interacting substances, such as zinc and sulfuric acid. During electrolysis electrical energy is consumed, the current being supplied by the battery. The production of a current may, therefore, be considered as the inverse of electrolysis.

Electrical energy may be produced by various chemical reactions, which are, in terms of the electronic theory, of one type, — oxidation (or loss of electrons) at one electrode, and reduction (or gain of electrons) at the other electrode. But before taking up the production of an electric current, a few common electrical units will be defined.

The **coulomb**,¹ as stated in a previous chapter, is the unit quantity of electricity. In one second one coulomb of electricity is transported past a given point by a current of one ampere. The **ampere** is represented by the current which will deposit silver from a solution of silver nitrate at the rate of 0.001118 g. per second. The **ohm**, the unit of resistance, is the resistance offered to a constant electric current by a column of mercury 106.3 centimeters in length having a cross section one millimeter square, at 0° C., and weighing 14.4 g. The **volt** is the unit of intensity. The potential difference between the electrodes (electromotive force, E.M.F.) is measured in volts.

In 1827 Ohm discovered an important law, which states that the electric current **C** is proportional to the voltage **E** and inversely proportional to the resistance **R**:

$$C = \frac{E}{R}; \text{ or, Amperes} = \frac{\text{Volts}}{\text{Ohms}}.$$

If a current is flowing and the voltage is doubled, the current (amperage) is doubled; but if the resistance is doubled, the current is halved.

¹ The electrical units owe their names to the following physicists: Coulomb (1736–1806), Ampere (1775–1836), Ohm (1787–1854), Volta (1745–1827), Joule (1818–1889), and Watt (1736–1819).

One volt is required to maintain a current of 1 ampere against a resistance of 1 ohm.

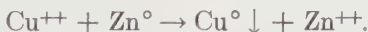
Electrical energy is the product of two factors — a quantity factor and an intensity factor:

Electrical Energy (expressed in Joules) = **Coulombs** \times **Volts**.
The product of the factors coulombs and volts expresses the quantity of electricity produced or consumed.

1 joule	= 1 volt-coulomb = 1 volt-ampere-second.
watts	= amperes \times volts.
1 watt	= 1 joule per second = 1 volt ampere.
1 joule	= 10,000,000 ergs. = 0.2391 cal.
1 watt	= 10,000,000 ergs. per second.
1 horse power	= 746 watts = 550 foot-pounds per second.
1 kilowatt	= 1,000 watts.

In commerce, 1 watt hour = 3,600 joules, and 1 kilowatt hour = 1,000 watt hours. The number of Amperes \times the number of Volts = Joules per second = Watts.

614. **The Production of an Electric Current.** — When a rod of such a metal as zinc is dipped into a solution of copper sulfate, the less active metal is displaced (126). Thus:



In terms of the electronic theory each atom of zinc gives up two electrons to the copper-ion. While there is a transfer of electrons, an electric current is not produced. In order to produce



FIG. 181. Salt Bridge.

a current it is necessary to carry out the reaction in vessels which prevent the copper-ion and the zinc from coming in contact. This may be accomplished by arranging the substances involved in the reaction



as shown in Fig. 181.

A solution of ZnSO_4 is poured into one beaker and a solution of CuSO_4 into another. A glass tube is filled with a solution of ZnSO_4 (or other suitable electrolyte), and the ends loosely stoppered with cotton (the so-called "salt bridge"). The ends of the glass tube are dipped into the solutions in the beakers, a rod of zinc dipped into the solution of ZnSO_4 , and one of copper into the solution of CuSO_4 . When the rods are joined to a galvanometer by means of wire, a current of electricity may be observed. Zinc goes into solution, forming the zinc-ion, Zn^{++} , and electrons flow through the wire and galvanometer to the copper and discharge the copper-ion:

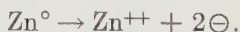


Metallic copper therefore deposits on the copper rod or plate. The salt bridge serves as a conductor between the solutions of the two salts.

(In the reaction just described, what is oxidized and what reduced?)

In order to produce an electric current by means of chemical reactions, the reactions are carried out in cells (Voltaic or Galvanic), which are commonly called batteries.¹

615. Cells or Batteries. — Volta, in 1800, produced a current by introducing a plate of zinc and one of copper into dilute sulfuric acid, and then joining the plates by means of a wire. According to the usual convention, the positive electricity is said to flow from the copper plate through the wire, to the zinc plate. *According to the electronic theory, however, negative electricity consisting of electrons flows in the opposite direction, i.e., from the zinc through the wire to the copper.* This is explained as follows: Metals are characterized by being able to go into solution in the form of positive ions; therefore, when zinc is immersed in dilute sulfuric acid, each atom of zinc loses two electrons, forming the zinc-ion:



The electrons thus liberated circulate through the wire to the copper plate, where they discharge the hydrogen-ion:



Gaseous hydrogen is therefore produced, which appears at the copper plate.

¹ Strictly speaking, a battery is a collection of cells.

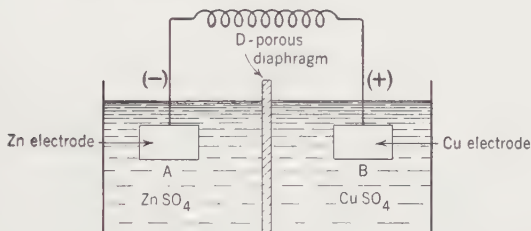
It is thus clear that the voltaic cell does not generate electricity. The electrons are associated with the atoms of zinc, from which they pass to the hydrogen ions. Electrons are driven round the outside conducting wire, energy being supplied by the battery.

The more active the metal, the greater is its tendency to lose electrons to form ions (126).

In the voltaic cell the metallic zinc is oxidized and the hydrogen-ion (H^+) reduced (why?).

The voltage of the voltaic cell is about 0.74. Davy used a battery of these cells, in 1807, for the electrolysis of the alkalis.

When the voltaic cell is in use, its voltage rapidly decreases, so cells of another type are employed. This type of cell may be illustrated by what is fundamentally the **Daniell cell** (Fig. 182).



(From "General Chemistry" by McCutcheon & Seltz.)

FIG. 182. Daniell Cell.

A vessel is divided into two compartments by means of a porous partition, and a solution of copper sulfate is introduced into one compartment and zinc sulfate into the other. Metallic copper is immersed in the cupric sulfate solution and zinc in the zinc sulfate, a wire being joined to each metal. When the circuit is open, electricity is not produced; but when the circuit is closed, a current flows through it. Zinc goes into solution, forming Zn^{++} , and an equivalent amount of Cu^{++} goes out of solution. The electrochemical change may be represented thus:



Copper is therefore deposited on the copper rod, and a stream of electrons circulates from the zinc through the wire to the copper, *i.e.*, an electric current is produced.

The concentration of Zn^{++} increases around the zinc, and that of $SO_4^{=}$ around the copper as the Cu^{++} is discharged. The

porous partition allows Zn^{++} to transmigrate, which keeps the solution electrically neutral as the reaction proceeds.

The arrangement in the Daniell cell is frequently represented as follows:



In general, in the production of a galvanic current, a porous partition (or an equivalent arrangement), *e.g.*, in the gravity cell, is employed to keep the two liquids apart. By keeping the liquids apart, electricity is produced instead of heat.

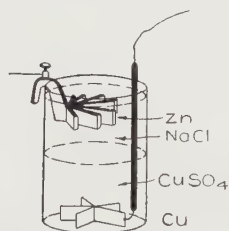


FIG. 183. Gravity Cell.

The reaction between zinc and cupric ions is often carried out by means of the **gravity cell** (Fig. 183). Zinc is placed in a solution of NaCl containing a very small quantity of the zinc-ion (Zn^{++}), and the copper is placed in a saturated solution of CuSO_4 . No partition is required. In practice, the jar is filled with salt solution and crystals of cupric sulfate are dropped

in. When the zinc and copper poles are connected, a current flows.

616. Electromotive Force; Single Potential Differences. — The electromotive force (E.M.F.) of a cell such as that just described, depends primarily upon the difference in the activity of the metals and upon the concentration of the ions. It is not affected, however, by changing the size or shape of the poles, nor by the mere quantity of the solutions.

When a metal is introduced into a solution of one of its salts, a difference of potential may be observed between the metal and the solution: *e.g.*, a rod of zinc placed in a normal solution of a zinc salt.

The electromotive force of a cell is the resultant of two effects. Thus, we have seen that when a rod of zinc is immersed in a solution of zinc sulfate, the metal has a tendency to pass into the ionic condition: $\text{Zn} \rightarrow \text{Zn}^{++} + 2\ominus$. The zinc-ion, on the other hand, has a tendency to take on electrons and to be discharged: $\text{Zn}^{++} + 2\ominus \rightarrow \text{Zn}^0$. In case the first tendency is stronger, a difference of potential results, the solution being positive with respect to the metal. If the second tendency is greater, the solution is negative with respect to the metal. The concentration of a solution is therefore an important factor in

determining the single potentials of metals in solutions of their ions.

In comparing potential differences, it is the general practice to introduce the metal into a solution containing 1 gram-equivalent of the metal-ion per liter. Inasmuch as it is not possible to determine absolute electrode potentials accurately, *it is customary to take as zero the potential of a platinized electrode saturated with hydrogen under a pressure of 1 atmosphere against a solution which is normal with respect to hydrogen-ion, and to refer other potentials to this as standard.* The values of some of the common metals are given in the table below. The potential differences of these metals against normal concentrations of their ions differ from that of hydrogen by the number of volts placed after the symbol. In this table hydrogen has a potential of zero, the metals above it in the electromotive series are negative, while those below it are positive.

POTENTIALS OF NORMAL SOLUTIONS IN CONTACT

K.....	-2.92	Fe(Fe++)...	-0.43	H ₂	0.00
Na.....	-2.72	Cd.....	-0.40	Cu(Cu++)..	+0.34
Mg.....	-1.55	Ni(Ni++)...	-0.22	Hg(Hg+)...	+0.79
Al.....	-1.34	Sn(Sn++)...	-0.14	Ag.....	+0.80
Zn.....	-0.76	Pb(Pb++) ..	-0.13	Hg(Hg++)..	+0.86

The more electropositive a metal, the greater is its tendency to lose electrons and the higher is its negative potential:



It is readily seen that the potential difference between two electrodes, in normal solutions of their ions, say, metallic zinc in normal zinc-ion solution and metallic copper in normal cupric-ion solutions, is the difference of the single potential differences. For zinc and copper it is 1.10 volts; for zinc is -0.76 volt and copper is $+0.34$ volt.

The E.M.F. of the Daniell or gravity cell is a little over 1 volt. The voltage increases as the difference between the activity of the metals increases.

The "normal potentials" of three of the halogens are as follows:

Chlorine.....	+1.35
Bromine.....	+1.08
Iodine.....	+0.62

617. Concentration Cells; Couples. — It has been stated that the difference of potential is altered by changing the concentration of the solutions. As a rule, the difference of potential between a metal and one of its ions is greater as dilution increases.

If two rods of zinc be dipped into a solution of zinc sulfate and the rods then connected by a wire, no current will be produced; but if the rods be placed in solutions of the zinc salt of different concentrations, a current will flow through the closed circuit. The difference of potential in a normal solution of zinc salt is 0.76, and in a more dilute solution (*e.g.*, 0.1 *N*), greater. The resultant pressure (or E.M.F.) of the combination is the difference of the two potentials. A cell such as the one just described is termed a concentration cell.

It has been pointed out that the rate of dissolution of zinc in sulfuric acid is augmented by bringing the zinc in contact with a less active metal, such as copper or platinum. Such a combination is known as a **couple**. A couple is virtually a short-circuited galvanic cell.

Tin-plate and *galvanized iron* are couples. The former consists of sheets of iron coated with tin. When damaged tin-plate is exposed to the atmosphere, it rusts rapidly. Iron and tin are in contact, being exposed to whatever electrolyte may be present. As iron is higher in the electromotive series, electrons flow from it to the tin; or the iron goes into solution as ions, which interact with carbonic acid to form ferrous carbonate, which is afterwards oxidized to ferric hydroxide.

When galvanized iron is exposed to the atmosphere, it is quite durable. Zinc and iron in the presence of moisture and carbonic acid are virtually a cell. Since zinc is higher in the electromotive series than is iron, it has a greater tendency to form ions, thus giving the insoluble carbonate, which serves as a protecting coat. Electrons flow from the zinc to the iron, so the former becomes the negative electrode, while the iron is the positive electrode. In case the material is damaged, however, the iron gradually corrodes.

It is well known that pure zinc dissolves very slowly in a dilute acid, due to the fact that the metal soon becomes coated with a layer of hydrogen, which protects it largely from further attack by the acid. By adding a small amount of a salt containing a metal lower in the electromotive series than zinc (*e.g.*, CoCl_2), the dissolution of zinc is greatly accelerated. The explanation is, that the more electronegative element is displaced by the zinc,

a couple being formed, which gives rise to galvanic action. The layer of hydrogen now shifts from the zinc to the more electro-negative metal (*e.g.*, Co, Cu, etc.), which exposes the zinc to the acid.

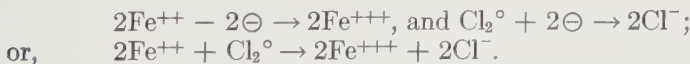
618. Electrolysis and Decomposition Potentials. — The application of the ionic theory to electrolysis has already been considered (233). In general, it may be stated that *when electrolysis is carried out, oxidation occurs at the anode and reduction at the cathode*. Faraday's laws governing electrolysis have already been discussed (229).

When the electrolyte cupric chloride is subjected to electrolysis, copper is liberated at the cathode and chlorine at the anode. If, after the electrolysis has been carried on for a time, the battery be removed and the wires joined, a current will be produced, which is called the *polarization current*. The copper and chlorine liberated at the electrodes form a sort of galvanic cell or battery. A counter E.M.F. is produced and is in operation during the entire electrolysis. In normal ionic concentration, its E.M.F. is $(1.35 - 0.34) = 1.01$ volts. This number is the decomposition potential of cupric chloride. In order to electrolyze this salt, an E.M.F. of at least 1.01 volts must be maintained in the battery. The decomposition potentials of other electrolytes, assuming normal ionic concentrations, may be readily calculated from the tables.

619. The Oxidation-Reduction Reaction. — It has been shown repeatedly that *oxidation consists in the loss of electrons by atoms or ions, while reduction is the converse* (263). Thus, when a solution of ferrous chloride is treated with chlorine, ferric chloride is formed:



In terms of the electronic theory, we have:



The electrons lost by the ferrous ions reduce a molecule of chlorine to the ionic condition. Chlorine is therefore the oxidizing agent, and the ferrous-ion the reducing agent. This may be regarded as a typical oxidation-reduction reaction.

Is it possible to produce electricity in the form of a current by an oxidation-reduction reaction? This may be accomplished by means of an oxidation-reduction cell. In case of the reaction just described, a solution of ferrous chloride is poured into one beaker

and chlorine water into another (together with some FeCl_3 to make the solution a conductor). The beakers are then connected by a salt bridge. Platinum electrodes are immersed in the two solutions and then joined to a galvanometer by wires (Fig. 184).

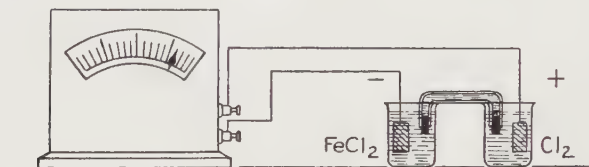


FIG. 184. Production of Electricity by the Oxidation-Reduction Reaction.

Electrons flow from the solution of ferrous chloride through the galvanometer to the solution of chlorine water, in which chlorine molecules are reduced to the chloride-ion:



Ferric chloride is formed, of course, in the other beaker. The platinum electrodes serve to carry the electrons out of and into the solutions. The deflection of the needle shows that an electric current is produced. Other oxidation-reduction reactions may be made to yield an electric current.

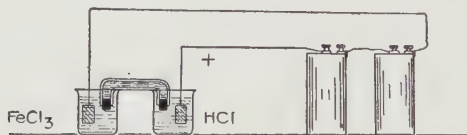


FIG. 185. Oxidation-Reduction by Means of the Electric Current.

Conversely, it is possible to bring about the oxidation-reduction reaction by means of the electric current. Two beakers and a salt bridge are arranged as in the experiment just described, but the beakers are filled with solutions of ferric chloride and hydrochloric acid respectively. A current from a battery of two dry cells is passed through the solutions, the electrode in the ferric chloride serving as cathode (Fig. 185). Each ferric-ion is reduced by an electron, a ferrous-ion being formed:



Ferrous chloride is therefore formed around the cathode. At the anode, the chloride ions are oxidized to free chlorine, which appears in the form of bubbles:



Note that the moving ions transfer the electricity through the solution from one electrode to the other, while the wire conducts the electrons from the battery.

Reducing Agents, or Oxidizable Substances.

(The higher the substance in this series, the greater is its activity as a reducing agent, or the more easily is it oxidized.)

Oxidizing Agents, or Reducible Substances.

(In descending this series the substances become more active oxidizing agents.)

K	\rightleftharpoons	K ⁺	+ \ominus
Na	\rightleftharpoons	Na ⁺	+ \ominus
Ca	\rightleftharpoons	Ca ⁺⁺	+ 2 \ominus
Mg	\rightleftharpoons	Mg ⁺⁺	+ 2 \ominus
Al	\rightleftharpoons	Al ⁺⁺⁺	+ 3 \ominus
Zn	\rightleftharpoons	Zn ⁺⁺	+ 2 \ominus
Fe	\rightleftharpoons	Fe ⁺⁺	+ 2 \ominus
Pb	\rightleftharpoons	Pb ⁺⁺	+ 2 \ominus
Sn	\rightleftharpoons	Sn ⁺⁺	+ 2 \ominus
H	\rightleftharpoons	H ⁺	+ \ominus
Cu	\rightleftharpoons	Cu ⁺⁺	+ 2 \ominus
2I ⁻	\rightleftharpoons	I ₂	+ 2 \ominus
Fe ⁺⁺	\rightleftharpoons	Fe ⁺⁺⁺	+ \ominus
Ag	\rightleftharpoons	Ag ⁺	+ \ominus
2Br ⁻	\rightleftharpoons	Br ₂	+ 2 \ominus
2Cl ⁻	\rightleftharpoons	Cl ₂	+ 2 \ominus
2Cr ⁺⁺⁺ + 7H ₂ O	\rightleftharpoons	Cr ₂ O ₇ ⁼	+ 14H ⁺ + 6 \ominus
Mn ⁺⁺ + 4H ₂ O	\rightleftharpoons	MnO ₄ ⁻	+ 8H ⁺ + 5 \ominus

The substances (*e.g.*, potassium and sodium) which are readily oxidized, are powerful reducing agents. Substances which are oxidized with difficulty are easier to reduce than those which are readily oxidizable: for example, copper is much more easily obtained by reduction than is magnesium or zinc.

620. The Hydrogen Electrode. — When a piece of platinum is coated with platinum black, it is able to adsorb on its surface a considerable quantity of hydrogen gas. By dipping such an electrode into a solution containing the hydrogen-ion (*e.g.*, hydrochloric acid) and then saturating the electrode with hydrogen gas at atmospheric pressure, we have what is called a *hydrogen*

electrode. Hydrogen molecules lose electrons, being transformed into hydrogen ions, while hydrogen ions tend to take on electrons to form molecular hydrogen:



The action is reversible, and equilibrium is attained between free hydrogen and hydrogen ions. This is analogous to the equilibrium attained between metallic copper and copper ions.

The **normal hydrogen electrode** may be produced by dipping the platinum electrode into a solution containing 1 gram-equivalent of hydrogen-ion per liter, and then saturating the electrode with hydrogen.

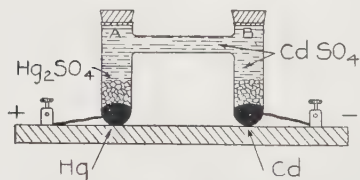


FIG. 186 Weston Standard Cell.

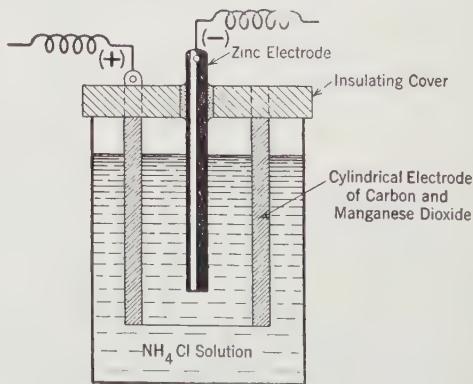
arriving at the end-point of titrations in solutions containing such highly colored substances that indicators cannot be used. Indeed, the hydrogen electrode is employed quite extensively in commercial laboratories for electrometric titration.

621. The Cadmium or Weston Standard Cell.—

This cell is employed for measuring E.M.F. One limb of the cell contains mercury at the bottom, which is connected through the glass to a binding post (+). Above the mercury there is a pasty mixture of mercurous sulfate and its saturated solution (Fig. 186).

On top of this and extending into the other limb of the cell there is a mixture of cadmium sulfate and its saturated solution. At the bottom of the limb there is

There are many practical applications of the hydrogen electrode, such as in determining the acidity of the fluids of the body in health and in illness; also for determining the extent to which solutions of certain salts hydrolyze; it is of further use in



(From "General Chemistry" by McCutcheon & Seltz.)

FIG. 187. Leclanché Cell.

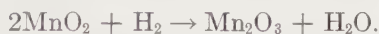
a button of cadmium or of cadmium amalgam, which is also connected to a binding post (-).

The Weston cell is very constant, giving a voltage of 1.0183 at 20°.

The **Leclanché cell** is of the irreversible type (Fig. 187); that is, polarization (618) is prevented. Electrodes of zinc and of carbon are immersed in a solution of ammonium chloride. The following changes occur at the electrodes:

- (1) $\text{Zn}^\circ \rightarrow \text{Zn}^{++} + 2\ominus$,
- (2) $2\text{NH}_4^+ + 2\ominus \rightarrow 2\text{NH}_3 + \text{H}_2$.

Electrons therefore circulate from the zinc to the carbon. Since hydrogen tends to collect on the carbon pole, it is oxidized by mixing manganese dioxide with the carbon:



Polarization is therefore prevented. The complete chemical change in the cell may be represented thus:



622. Dry Cells. — The so-called “dry” cells are produced on a very large scale, being employed for bells, flash-lights (electric torches), telephones, radio-sets, etc. The word “dry” is not appropriate; for if the contents of the cell were really dry, it would not function. Instead of containing a fluid, the cells contain a moist mixture in the form of a paste, and can therefore be transported more conveniently than can those containing liquids. A section of a very common dry cell is shown in Fig. 188. A carbon rod constitutes the positive electrode, and it is packed

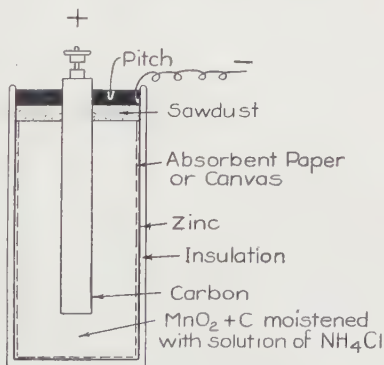


FIG. 188. Dry Cell.

in a mixture of manganese dioxide, graphite and crushed charcoal, moistened with a solution of ammonium chloride, often mixed with zinc chloride. A zinc can serves as the negative electrode, the can being separated from the manganese dioxide mixture by

absorbent paper, pulpboard, or a muslin bag. Sawdust or sand is placed above the manganese dioxide mixture, and the top of the apparatus is sealed with wax or pitch. When the cell is operated, zinc goes into the ionic state at the negative electrode; hydrogen is also formed, but is oxidized by the manganese dioxide and not liberated at the positive electrode. (What effect would the hydrogen have if it were liberated at the positive electrode?) The dry cell, when fresh, has a voltage of about 1.5. When a good dry cell is allowed to rest, it should recover its E.M.F. (why?). In the course of time, however, dry cells deteriorate, and must be replaced.

The *storage cell*, or *lead accumulator*, has already received attention (611).

EXERCISES

1. State the theory of the production of the electric current from chemicals. Draw and explain a diagram of an electric cell.

2. Electric energy is the product of what two factors? State it mathematically. State Ohm's law.

3. What is the relation of watts to amperes and volts? What is a horse power?

4. Define, in terms of the electronic theory, the oxidation-reduction reaction, and apply it to (1) the Daniell cell, and (2) the electrolysis of a solution of silver sulfate between silver electrodes.

5. Explain the following: (1) why pure zinc is not attacked readily by dilute acids; (2) the action of any metallic couple; (3) why zinc rods and plates used in electric cells are covered with mercury ("amalgamated"); (4) single potential differences produced by metals; (5) polarization current: *e.g.*, when hydrochloric acid is electrolyzed.

6. Explain (1) how an electric current may be produced by means of an oxidation-reduction cell, and (2) how it is possible to carry out the oxidation-reduction reaction by employing a dry battery.

7. (a) State Faraday's law and show its application. How many coulombs would be required to deposit 5 g. of copper from a solution of copper sulfate?

(b) Two cells with platinum electrodes, one containing dilute sulfuric acid and the other cupric sulfate, are connected in series, and an electric current passed through them. When 0.5 g. of hydrogen has been released in the first cell, what weight of copper has been deposited in the second cell?

8. How much time would be required to deposit 0.1 g. of cadmium by passing a current of 1 coulomb per second through the solution?

9. What determines the amount of current produced by a cell? What determines the voltage?

10. In setting up a cell, what is the function of the so-called salt bridge?

11. What is the relation of the tendency of atoms of metals to lose electrons to their position in the electrochemical series?

12. If you were given zinc, silver, zinc sulfate, and silver sulfate, how would you proceed to produce an electric current?

13. Explain the action of any dry battery.
14. What is meant by a concentration cell and what determines its voltage?
15. In terms of the ionic theory, state all the differences you can between 0.1 *N* solutions of hydrochloric and acetic acids.
16. What is meant by the hydrogen electrode? the normal hydrogen electrode? Mention some applications of the hydrogen electrode.
17. Review the chemistry of the storage cell.

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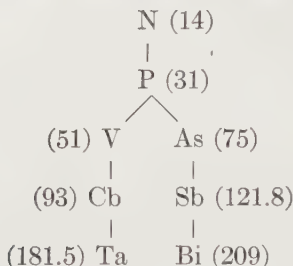
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CHAPTER XXXV

THE ARSENIC GROUP

623. **General Characteristics and Relationships.** — The members of the Arsenic Group are *arsenic*, *antimony*, and *bismuth*. These elements constitute Sub-group B of Group V of the Periodic System, as shown by the accompanying diagram.



According to this arrangement, nitrogen and phosphorus may be regarded as linking vanadium, columbium, and tantalum to the arsenic group.

Arsenic, antimony, and bismuth are often treated as members of the nitrogen or phosphorus family. While this is logical, it is true that in analysis quite a sharp line can be drawn between nitrogen and phosphorus on the one hand and the arsenic group on the other hand. Since nitrogen and phosphorus are strictly acidic and the elements of the arsenic group possess some well-defined metallic characteristics, the latter are classed with the metals in the scheme of qualitative analysis.

Nitrogen forms much stronger acids than do carbon and silicon of Group IV. Likewise, phosphorus enters into the formation of acids, but they are not as strong as nitric acid. In going from nitrogen to bismuth the electropositive character of the element becomes more pronounced and the acidic character of the analogous acids diminishes. In general, it may be stated that *the more electropositive an element, the less acidic, or the more basic, is its hydroxide*: for example, phosphorus hydroxide or phosphorous acid, P(OH)_3 , is strictly acidic; but arsenious hydroxide or arsenious acid, As(OH)_3 , is amphoteric in character; that is, it is both acidic and basic.

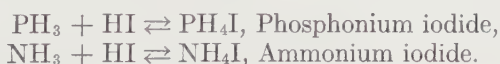
As a rule, non-metals form stable, gaseous hydrides. The elements of Group V form the following well-known hydrides, all of which are colorless gases:



The transition from non-metal to metal is well illustrated in passing from nitrogen to bismuth. The heat of formation of the hydride decreases from nitrogen to antimony, that of arsine and stibine being negative. The stability of the hydride therefore decreases with increase in the atomic weight of the element. As arsine and stibine have negative heats of formation, or are endothermic compounds, they are relatively unstable. Ammonia decomposes rapidly at $1,300^\circ$, while stibine decomposes rapidly at 150° . It appears that bismuth forms a hydride, but not much is known about it.

These unstable hydrides are strong reducing agents, and they have a pronounced poisonous character, arsine being extremely poisonous. They also are combustible.

Phosphine, like ammonia, has basic properties, giving rise to **phosphonium compounds**, which are analogous to ammonium compounds, but much less stable:



The following table shows some of the striking family relationships of the members of the Nitrogen Family.

THE ELEMENTS OF THE NITROGEN FAMILY

	Nitrogen N	Phosphorus P	Arsenic As	Antimony Sb	Bismuth Bi
Atomic weight.	14.008	31.027	74.96	121.77	209.0
Melting point..	-210.5°	44°	850° (in sealed tube)	630°	271°
Sp. gr. (solid)..	1.0265	1.83	5.73	6.7	9.8
Hydrides.....	NH_3	PH_3	AsH_3	SbH_3
Chlorides.....	NCl_3	PCl_3	AsCl_3	SbCl_3	BiCl_3
Oxides.....	N_2O_3	P_2O_3	As_2O_3	Sb_2O_3	Bi_2O_3
	N_2O_5	P_2O_5	As_2O_5	Sb_2O_5	Bi_2O_5
	HNO_3	HPO_3	HAsO_3	HSbO_3
Acids.....	H_3PO_3	H_3AsO_3	H_3SbO_3
	H_3PO_4	H_3AsO_4	H_3SbO_4
	$\text{H}_4\text{P}_2\text{O}_7$	$\text{H}_4\text{As}_2\text{O}_7$	$\text{H}_4\text{Sb}_2\text{O}_7$

It should be noted that the element, in accordance with the general rule, becomes more basic with increasing atomic weight. In this family of elements we pass from nitrogen, a colorless gas, to bismuth, a heavy brittle metal.

The three elements of the Arsenic Group exhibit a gradation of properties. Non-metallic properties predominate in arsenic, and metallic in bismuth. Arsenic and its compounds closely resemble phosphorus and its compounds, and antimony has a similar relation to arsenic. Bismuth, however, is very different in many respects. Thus, its oxides are much more basic, and its hydride is very unstable. Its salts, like those of antimony, are partially hydrolyzed by water, which shows that it is not strongly basic. Moreover, bismuth is brittle. It is not, therefore, a typical metal as are silver and sodium.

Arsenic and antimony, like phosphorus, exist in allotropic modifications, which differ in density.

The elements of Sub-group V A — *vanadium*, *columbium*, and *tantalum* — are metallic elements. Vanadium forms a number of types of compounds which are analogous to those of nitrogen and of phosphorus, especially the latter. In vanadium, however, metallic properties predominate. Columbium and tantalum are somewhat rare, and are noteworthy in that basic oxides (M_2O_3) of these metals are unknown. Their chief compounds are columbates and tantalates. Apparently neither of these metals forms salts with acids. Their pentoxides (M_2O_5) are feebly acidic.

ARSENIC. As = 74.96

624. History and Occurrence. — The ancients were acquainted with the yellow and red sulfides of arsenic, and “white arsenic” (As_2O_3) and free arsenic were known to the Greek alchemists. The word arsenic is derived from a Greek word meaning masculine or potent.

Arsenic occurs quite widely distributed in nature, usually in combination with sulfur, or a metal, or both. The most important of its ores is

Arsenopyrite or Mispickel. $FeAsS$

This mineral is mined at several places in Virginia and in the state of Washington. Arsenic also occurs in the form of the sulfides —

	Realgar (red).....	As_2S_2
and	Orpiment (yellow).....	As_2S_3 .

These sulfides have been known since the time of Aristotle.

Arsenious oxide occurs in nature as the mineral

Arsenolite.....	As_2O_3 .
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Arsenic also occurs in ores of copper, silver, gold, nickel, cobalt, etc., such as

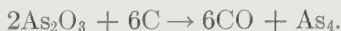
Smaltite.....	CoAs_2
Niccolite.....	NiAs
Cobaltite.....	CoAsS
Enargite.....	Cu_3AsS_4
Proustite.....	Ag_3AsS_3 .

Most of the arsenic for commercial purposes is obtained in the form of arsenic trioxide, or "white arsenic," from the flue-dust of smelters treating such ores. Arsenic thus obtained is known as a by-product of metallurgical works. In some plants the electrostatic precipitation method is employed for the recovery of "white arsenic," which increases the yield and improves the condition of the atmosphere (477). Free arsenic occurs in limited amounts in nature.

625. Preparation. — Arsenic is prepared by heating *arsenopyrite*, the air being excluded:



The arsenic sublimes into iron tubes, and is obtained as a brittle, crystalline mass having a metallic appearance. Arsenic also is prepared by reducing arsenious oxide with carbon. In Silesia this reduction is carried out in crucibles covered with a conical iron cap, and in the laboratory by heating the mixture in a glass tube closed at one end:



Arsenic is readily purified by sublimation.

626. Properties. — Arsenic is a brittle, steel-gray, crystalline solid having the appearance of a metal. Its specific gravity at 14° is 5.727. Allotropic forms of arsenic are known, however, so its density is variable. When arsenic is heated under ordinary conditions, it forms a vapor without melting. The vapor is of a

lemon-yellow color and has the odor of garlic. At 644° the vapor consists of tetratomic molecules (As_4), but at $1,700^{\circ}$ the molecules are diatomic (As_2).

When arsenic is heated in oxygen, it burns with a bright white flame, forming arsenious oxide; it also burns in air, forming the same compound. Arsenic also combines with the halogens, sulfur, and many of the metals. Arsenides are analogous to nitrides and phosphides. Concentrated nitric acid oxidizes arsenic to arsenic acid. This reaction indicates that arsenic is acidic in nature. While it has some of the properties of a metal, it possesses more of the properties of a non-metal. Chemically, arsenic closely resembles phosphorus.

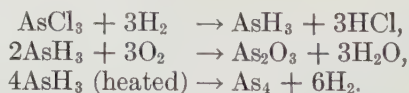
Arsenic is used in hardening metals; particularly in the manufacture of lead shot (603).

COMPOUNDS OF ARSENIC

Arsenic forms many compounds which are very similar to those of phosphorus. Both elements have valences of 3 and 5. The compounds of arsenic may be divided into Arsenious Compounds and Arsenic Compounds. The former correspond to As_2O_3 and the latter to As_2O_5 . A few of the most interesting and important arsenic compounds will be considered.

627. Arsine, or Hydrogen Arsenide, AsH_3 . — This compound (compare NH_3 and PH_3) may be formed in small quantity by pouring two or three drops of a solution of an arsenic compound (*e.g.*, AsCl_3) into a hydrogen generator in which zinc and dilute hydrochloric acid are interacting. Arsine is dried by passing the gas through calcium chloride, and it may be ignited at the end of the delivery tube as shown in Fig. 189; it burns with a bluish-white flame. By introducing a clean porcelain dish into the flame, a metallic-appearing deposit of arsenic is obtained; and by heating the tube in front of a constriction, arsenic deposits in the constricted portion. This is known as **Marsh's test**, and it is exceedingly delicate.

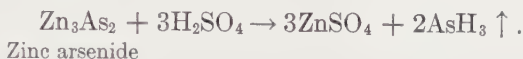
The chemical changes are as follows:



Arsine is very poisonous! Great care must be exercised in preparing this gas. Gehlen, in 1815, lost his life by breathing an ex-

ceedingly small amount of it. Arsine has a peculiar and disagreeable odor. Unlike NH_3 and PH_3 , it forms no compounds with halogen acids.

Arsine also is formed by the action of dilute acids upon *arsenides* of metals:



Certain arsenides also tend to hydrolyze, forming arsine. This action may be compared with that of water upon phosphides (*e.g.*, Ca_3P_2) and nitrides (*e.g.*, Mg_3N_2).

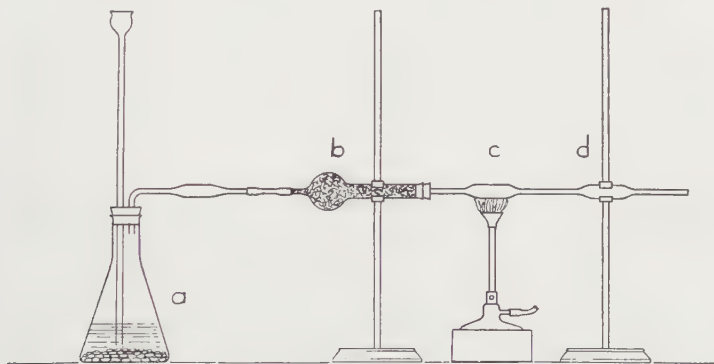


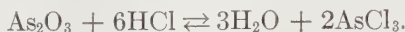
FIG. 189.

628. Oxides of Arsenic. — Arsenic forms two common oxides: Arsenious oxide or arsenious anhydride, As_2O_3 (As_4O_6), and Arsenic pentoxide or arsenic anhydride, As_2O_5 .

Arsenious oxide, the most important compound of arsenic, is often called "white arsenic," or simply "arsenic." Its vapor density up to $1,500^\circ$ shows that its formula is As_4O_6 , but the simpler formula As_2O_3 is generally used. As stated before, much arsenic trioxide is obtained as a by-product of metallurgical operations. It is produced in quantity by roasting or calcining mispickel (FeSAs). The ore is heated in a calciner or furnace, and the gases from the furnace are conducted through dust-catchers, much of the arsenic trioxide being deposited. This oxide is known in more than one form.

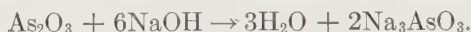
Arsenious oxide is appreciably soluble in water, about 1 part of the oxide dissolving in 50 parts of water at 25° . The solution

contains arsenious acid (H_3AsO_3). Arsenious oxide dissolves in hydrochloric acid, forming arsenic trichloride:



In this reaction the oxide is basic in character (compare with this the action of HCl on CaO).

When heated with a solution of sodium hydroxide, it forms sodium arsenite, in which arsenic functions as a non-metal:



In this reaction arsenious oxide is acidic. The oxide (or hydroxide) is therefore amphoteric in character. In other words, arsenic has some of the properties of a metal and some of those of a non-metal.

Arsenious oxide is a reducing agent. Large quantities of arsenious oxide are used as an insecticide and weed killer; for preserving skins and furs; and in the manufacture of opaque glass and enamels.

A solution of arsenious oxide is a powerful poison, 2-4 grains usually being a fatal dose. Freshly precipitated ferric hydroxide or magnesium hydroxide is a good antidote. A person can accustom himself to sustain the action of quantities of arsenic that would ordinarily prove fatal. It is said on good authority that arsenic-eating occurs in Styria. According to Roscoe, "a wood-cutter was seen by a medical man to eat a piece of pure arsenious oxide weighing 4.5 grains, and the next day he crushed and swallowed another piece weighing 5.5 grains, living on the following day in his usual state of health." Arsenic-eaters claim that the substance enables them to carry heavy loads to great elevations with ease.

Arsenic pentoxide, As_2O_5 , may be obtained as a white porous mass by heating arsenic acid to a temperature slightly below redness:



It interacts with water to form arsenic acid.

629. Oxygen Acids of Arsenic. — The acids of arsenic are analogous to those of phosphorus, but are weaker and not so stable.

Arsenious acid, H_3AsO_3 , is known only in solution. It is formed by treating arsenious oxide with water:



The acid is weak and unstable, and its salts are called **arsenites**. Soluble arsenites are very poisonous. Arsenious oxide and arsen-

ites are used in small doses in medicine. "Fowler's solution" contains potassium arsenite. **Paris green** is arsenite and acetate of copper (a double salt); it is used as an insecticide. **Scheele's green** has the formula CuHAsO_3 .

Arsenious acid is a reducing agent and is therefore employed in volumetric analysis. Thus, a standard solution of arsenious acid may be used in the determination of halogens: for example, the "available" chlorine in bleaching powder. On the other hand, a standard solution of iodine may be employed to determine arsenious acid.

The principle upon which the method of analysis is based is the fact, that when arsenious acid is treated with oxidizing agents such, for example, as the elements of the chlorine family, it is converted into arsenic acid:



As a matter of fact the determination is made in the presence of water and a free alkali or an alkali salt, so the chemical change involved is substantially as follows:



The alkali must be present in sufficient quantity to combine with the HI formed.

Orthoarsenic acid (H_3AsO_4), **pyroarsenic acid** ($\text{H}_4\text{As}_2\text{O}_7$), and **metarsenic acid** (HAsO_3) correspond to the phosphoric acids. As_2O_5 is the anhydride of these acids. Salts of orthoarsenic acid are called **orthoarsenates**, or simply **arsenates**. Soluble arsenates are very poisonous. *Lead arsenate* is extensively used for spraying fruit trees, the commercial product usually being a mixture of $\text{Pb}_3(\text{AsO}_4)_2$ and PbHAsO_4 . *Sodium arsenate*, $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$, is used in calico-printing, and *calcium arsenate* for exterminating the boll-weevil which infests the cotton-boll. A neutral solution of an arsenate produces with silver nitrate a reddish-brown precipitate of Ag_3AsO_4 .

Arsenic acid is stronger than arsenious acid, just as nitric acid is stronger than nitrous acid. This is an illustration of the general fact that whenever an element enters into the formation of more than one oxygen acid, the acid in which the element has the highest positive valence is the strongest.

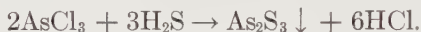
630. Sulfides of Arsenic. — **Arsenic disulfide**, As_2S_2 , occurs as the mineral realgar. It can be prepared as a red, vitreous mass

by fusing together arsenic and sulfur. As_2S_2 is employed in the manufacture of "white-fire," or "Bengal Lights," and in tanning.

T. L. Shear discovered in 1927, in the excavations at Corinth, a crude pot containing a red pigment, which was chemically analyzed by the writer and found to be realgar. Objects lying in the vicinity of the pot belong to the end of the fifth or the beginning of the fourth century B.C.

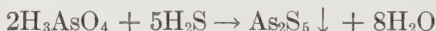
At Corinth the pigment was apparently dedicated as an appropriate and valuable offering to the Goddess Athena.

Arsenic trisulfide, As_2S_3 , occurs in nature as the mineral orpiment. It can be prepared as a fine yellow precipitate by passing hydrogen sulfide into a solution of As_2O_3 in hydrochloric acid:

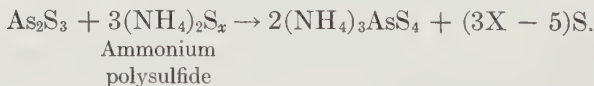
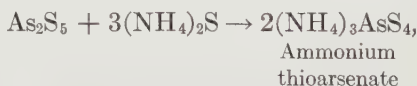


The compound is insoluble in water. When As_2O_3 is dissolved in water and then treated with pure hydrogen sulfide, a liquid with a yellow color is obtained. Arsenic trisulfide is formed, but is present in colloidal form; it may be coagulated by adding an acid to the liquid.

Arsenic pentasulfide, As_2S_5 , can be obtained as a yellow precipitate by saturating a strong hydrochloric acid solution of quinquevalent arsenic, kept cold, with a rapid stream of H_2S :



Thioarsenates (or **sulfarsenates**) are formed by dissolving As_2S_5 in a solution of a sulfide of ammonium or an alkali metal, or by treating As_2S_3 with a polysulfide:



The salts of thioarsenic acid are decomposed by acids, the pentasulfide being precipitated and hydrogen sulfide formed:



Arsenic trisulfide dissolves in ammonium sulfide to form *ammonium thioarsenite*, a salt of the acid H_3AsS_3 :



This salt yields As_2S_3 when treated with an acid (write equation). The sulfides of ammonium are therefore important in analytical chemistry for separating the metals of the arsenic group (see Antimony and Tin) from certain other metals.

When a solution of arsenic acid is treated with a slow current of H_2S , the precipitate is not pure arsenic pentasulfide, but a mixture of this compound with arsenic trisulfide and sulfur. According to the old hypothesis of Rose (which is wrong), arsenic acid is reduced by hydrogen sulfide directly to arsenious acid, which interacts with more H_2S to form As_2S_3 :



L. W. McCay has shown that *arsenic acid is never reduced by H_2S directly to arsenious acid and free sulfur*. His experiments have proved that monosulfoxyarsenic acid ($\text{H}_3\text{AsO}_3\text{S}$) is first formed, which loses sulfur, and then interacts with more H_2S to form As_2S_3 . These changes may be formulated thus:



McCay's results have been confirmed by the author (*J. Am. Chem. Soc.*, XXXVIII, I (1916)).

631. Thioarsenic Acids.—Oxygen and sulfur belong to the same family; therefore atoms of sulfur may displace atoms of oxygen in certain compounds. The series of acids from arsenic acid to thioarsenic acid is a beautiful illustration of this fact, which is shown in the following table. The acids are sometimes called sulfoxyarsenic acids.

Name of Acid	Formula	State of Acid	Tertiary Sodium Salt	Discoverer of Acid
Arsenic acid.....	H_3AsO_4	White solid.	$\text{Na}_3\text{AsO}_4 \cdot 12\text{H}_2\text{O}$	Scheele
Monothioarsenic acid....	$\text{H}_3\text{AsO}_3\text{S}$	Known only in dilute solution.	$\text{Na}_3\text{AsO}_3\text{S} \cdot 12\text{H}_2\text{O}$	McCay
Dithioarsenic acid.....	$\text{H}_3\text{AsO}_2\text{S}_2$	Known only in very dilute solution.	$\text{Na}_3\text{AsO}_2\text{S}_2 \cdot 11\text{H}_2\text{O}$	Preis and McCay
Trithioarsenic acid.....	H_3AsOS_3	Unknown in free state.	$\text{Na}_3\text{AsOS}_3 \cdot 11\text{H}_2\text{O}$	McCay and Foster
Thioarsenic acid.....	H_3AsS_4	Unknown in free state.	$\text{Na}_3\text{AsS}_4 \cdot 8\text{H}_2\text{O}$	Berzelius

ANTIMONY. Sb = 121.77

632. **History and Occurrence.** — Antimony occurs in nature chiefly as the mineral **stibnite** or **antimony glance**, Sb_2S_3 (Fig. 190). This compound was used in very early times by Oriental women for painting the eyebrows. Paracelsus and other iatrochemists (p. 7) were acquainted with many preparations containing antimony. Indeed, the use of antimony in medicine was



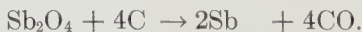
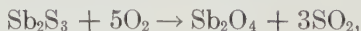
(American Museum of Natural History.)

FIG. 190. Stibnite Crystals, Mt. Kosang, Japan.

quite the vogue in the days of the medical chemists. A book entitled the "Triumphal Car of Antimony" was published early in the seventeenth century.

Antimony occurs principally in the Pacific ore-circle and around the Mediterranean Sea. By far the most valuable deposits occur in China. The United States imports most of the antimony used in our industries, but some "antimonial lead" is produced as a by-product of the lead-smelting industry. Antimony occurs in small quantities in the free state.

633. **Preparation.** — (1) Antimony can be prepared by roasting stibnite and then reducing the oxide with carbon:



The reduction is carried out in graphite crucibles.

(2) By heating Sb_2S_3 and metallic iron in graphite crucibles:



The crude metal separates from the slag (chiefly FeS) and is purified by heating with a small quantity of clean stibnite.

634. Properties. — Antimony is a hard, brittle, silver-white crystalline solid, having a specific gravity of 6.7 and a melting point of 630° . When heated in air, the metal burns with a bluish flame, forming Sb_2O_3 (or Sb_2O_4). If a small globule of antimony be thrown on a piece of paper with upturned edges, it breaks up into many smaller globules each of which skips about on the paper, burning all the while, and leaving very regularly marked hyperbolic trails. At $1,640^\circ$ the molecular formula is Sb_2 , but at lower temperatures Sb_4 is present. Antimony has allotropic forms, the most peculiar and interesting of which is "explosive antimony"; it may be obtained by the electrolysis of a solution of antimony trichloride. When this form of antimony is heated to 200° , it explodes sharply, forming a fine powder; it also breaks down when scratched with a metallic point or when touched with a red-hot wire. Antimony combines directly with the halogens, and is oxidized by strong nitric acid. It is an amphoteric element, but is more basic than is arsenic.

COMPOUNDS OF ANTIMONY

The compounds of antimony correspond, in general, to those of arsenic, which resemble phosphorus compounds.

635. Stibine, SbH_3 . — The hydride of antimony is formed by the action of zinc and hydrochloric acid on a soluble compound of antimony, such as SbCl_3 . This is analogous to the formation of arsine (627). Stibine is a colorless, poisonous gas, and it burns with a greenish-white flame and decomposes when heated, forming a sooty deposit of metallic antimony. This deposit, unlike that of arsenic, is involatile when heated with the Bunsen flame, and is insoluble in a solution of bleaching powder.

636. Oxides and Acids. — The oxides and acids of antimony are very similar to those of arsenic. The following oxides of antimony are known:

Antimony trioxide, Sb_2O_3 (or Sb_4O_6),
Antimony tetroxide, Sb_2O_4 ,
Antimony pentoxide, Sb_2O_5 .

All these oxides are acidic in nature, and the trioxide is also weakly basic.

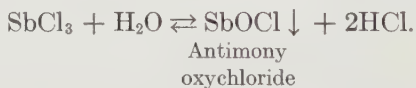
Antimony trioxide is a white compound which may be obtained by heating the metal or its sulfide in air; it also may be formed by oxidizing the metal with nitric acid. By treating this oxide with certain acids, salts may be formed, such as $\text{Sb}(\text{NO}_3)_3$ and $\text{Sb}_2(\text{SO}_4)_3$. This oxide is the anhydride of antimonious acid (H_3SbO_3), and it may be oxidized to antimonic acid by the action of suitable oxidizing agents. $\text{Sb}(\text{OH})_3$ is an amphoteric hydroxide (566).

Antimony tetroxide, Sb_2O_4 , may be obtained as a white powder by heating either of the other oxides to a high temperature in the presence of air. Some chemists claim that this oxide is neither basic nor acidic, and they regard it as antimony antimonate (SbSbO_4).

Antimony pentoxide, Sb_2O_5 , may be obtained as light yellow powder by rapidly evaporating the powdered metal or its lower oxide with nitric acid, followed by gentle ignition of the residue (compare it with P_2O_5 and As_2O_5).

637. Halides of Antimony. — Antimony forms halides of the types SbX_3 and SbX_5 . These salts, like other salts of antimony, are partially hydrolyzed by water, yielding basic salts.

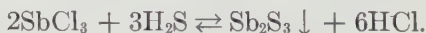
Antimony trichloride, an old name for which is "butter of antimony," may be produced by heating an excess of metallic antimony, or its sulfide, in a current of dry chlorine. A solution of the salt may be obtained by boiling the sulfide with strong hydrochloric acid. When treated with water, the salt hydrolyzes, yielding a white precipitate:



Antimony trichloride is used for giving a brown stain to iron and steel wares, such as gun-barrels.

638. Sulfides of Antimony. — The sulfides of antimony (Sb_2S_3 and Sb_2S_5) are very similar to the corresponding sulfides of arsenic, but they are orange-red in color. They dissolve in sulfides of the alkali metals to form thio-salts (see Arsenic, 630).

Antimony trisulfide occurs in nature as stibnite, which is black. The compound may be obtained as an orange-red precipitate by treating an antimonous salt with hydrogen sulfide:



The compound is practically insoluble in dilute hydrochloric acid. When heated to 200° , this salt turns black.

Antimony pentasulfide is formed when a thioantimonate is treated with an acid (see Arsenic). This compound resembles the trisulfide, but is unstable.

The sulfides of antimony are used in the production of red rubber.

639. Other Compounds of Antimony. — One of the most important salts of antimony is **tartar emetic** or **antimonyl potassium tartrate**, $(\text{SbO})\text{KC}_4\text{H}_4\text{O}_6 \cdot 1/2\text{H}_2\text{O}$. It is a white solid and is soluble in water. The salt has been used in medicine for a very long time; it also is used as a mordant in dyeing. The radical antimonyl $(\text{SbO})^+$ is present in a large number of basic salts of antimony.

Antimony sulfate, $\text{Sb}_2(\text{SO}_4)_3$, may be formed by treating antimony with concentrated sulfuric acid.

Sodium pyroantimonate, $\text{Na}_2\text{H}_2\text{Sb}_2\text{O}_7$, is very sparingly soluble in water (see Sodium Compounds).

640. Uses of Antimony. — Antimony forms alloys with most heavy metals, and the alloys are harder than the pure metals. On solidifying, most of these alloys of antimony slightly expand. **Type metal** is an alloy of antimony, lead, and tin; **Britannia metal**, used in making cheap tableware, etc., is an alloy of antimony, tin, copper, and zinc; **Babbitt (antifriction) metal** is usually an alloy of antimony, tin, and copper.

The red sulfides of antimony are employed as paint pigments and in vulcanizing and coloring red rubber.

White antimony oxide (chiefly Sb_2O_3) is used in the manufacture of opaque white enamel and other sanitary ware.

Antimony sulfide is used in the manufacture of matches and as a component of primers in shells and cartridges.

Certain antimony compounds, such as tartar emetic, are also used in medicine. When taken internally, they act as a depressant of the heart.

BISMUTH. Bi = 209

641. Occurrence and Preparation. — Bismuth occurs in Bolivia, Saxony, Bohemia, Peru, Chile, the United States, and in some other countries. It is not abundant, but is rather widely scattered in mineral regions. The metal occurs chiefly in the free state; but minerals, such as **bismuth glance** (Bi_2S_3) and **bismuth ochre** (Bi_2O_3), are found. In the year 1918 the United States imported 135,700 pounds of bismuth. Bismuth was known in the Middle Ages,

but as it was impure there was considerable confusion as to its real nature. It appears that the metal itself was not used during that period.

Bismuth may be prepared by roasting the sulfide in a furnace and then reducing the oxide with carbon and a suitable flux.

Large quantities of the metal are obtained from "bismuth concentrate": for example, the concentrate is obtained as a by-product of the concentration of tin ores mined in Bolivia. When bismuth is in the free state, it may be obtained by heating the concentrate until the metal melts; it flows away leaving the matrix behind. Bismuth also is produced from anode slimes derived from the electrolytic refining of copper and lead (see the Betts process).

642. Properties. — Bismuth is a shining, brittle, gray-white, crystalline metal with a ruddy tint. The metal has a specific gravity of about 9.8, and melts at 271° . The thermal conductivity of bismuth is 18, while that of silver is 1,000. It has the lowest thermal conductivity of all the metals. Bismuth has an electrical conductivity of 1.2, that of silver being 100. Bismuth is the most diamagnetic substance known. On account of its thermoelectric properties it is especially valuable for the construction of thermopiles. The metal expands on cooling, which renders it very useful in the production of certain alloys, such as type metal. When heated, it burns in air to form Bi_2O_3 . Unlike the other elements of the phosphorus family, bismuth has no acidic properties; it is found in no acids, but is exclusively basic in character, yet rather weakly so. Bismuth dissolves in hot concentrated nitric and sulfuric acids, forming salts in which it has a valence of 3 — $\text{Bi}(\text{NO}_3)_3$ and $\text{Bi}_2(\text{SO}_4)_3$.

643. Uses of Bismuth. — Bismuth is used in the manufacture of fusible alloys: *e.g.*, **Wood's metal** and **Rose's metal**. Wood's metal contains 4 parts of bismuth, 2 of lead, 1 of tin, and 1 of cadmium, and melts at 60.5° . Rose's metal contains 2 parts of bismuth, 1 of lead, and 1 of tin; it melts at 93.8° . These fusible alloys are used in the manufacture of safety plugs in boilers, automatic fire curtains, water sprinklers, etc. These alloys of bismuth are a good illustration of the general rule that an alloy has a lower melting point than its constituent metals. In other words, the melting point of pure metals may be lowered by adding foreign metals. "Bismuth subnitrate" and bismuth carbonate are used in quantity in medicine.

644. Compounds of Bismuth. — **Bismuth trioxide** is obtained as a yellow powder by oxidizing the metal or by heating the nitrate

or hydroxide. This oxide is more basigenic than antimony trioxide, and forms a well-defined series of salts.

Bismuth trisulfide may be produced as a brown-black precipitate by treating a solution of a bismuth salt with hydrogen sulfide. The compound is soluble in hot dilute nitric acid, but insoluble in the sulfides of ammonium (see Arsenic and Antimony).

Salts of bismuth, like those of antimony, undergo partial hydrolysis in water, giving basic salts. Thus, when a few drops of a solution of bismuth chloride are poured into a beaker of water, a white precipitate of bismuth oxychloride forms (637):



Bismuth subnitrate, $\text{Bi}(\text{OH})_2\text{NO}_3$, a basic salt, is used in medicine as an internal remedy in the case of certain intestinal and stomach disorders. It also is used in cosmetics. When dried, the salt has a tendency to lose water, forming $(\text{BiO})\text{NO}_3$. The **bismuthyl radical** (BiO) has a valence of 1.

Bismuth carbonate and the basic nitrate are consumed in connection with the X-ray examination of the oesophagus and stomach. Bismuth is nearly opaque to X-rays, due to its high atomic weight.

645. Analytical. — Acid solutions of salts of the metals of the Arsenic Group are precipitated as sulfides by hydrogen sulfide. *Bismuth sulfide* (Bi_2S_3) is insoluble in ammonium sulfide, while the sulfides of arsenic and of antimony are soluble. Bi_2S_3 is soluble in nitric acid, forming $\text{Bi}(\text{NO}_3)_3$. When a solution of a bismuth salt is treated with ammonium hydroxide, a white precipitate of bismuth hydroxide is formed, which readily dissolves in hydrochloric acid. The presence of bismuth can be confirmed by pouring a solution of BiCl_3 into much water; the liquid assumes a milky appearance. The sulfides of arsenic (As_2S_3 and As_2S_5) are yellow, and the corresponding compounds of antimony are orange-red (see Tin). The Marsh test enables the chemist to detect exceedingly small quantities of arsenic and antimony. The cations of the elements of the Arsenic Group are colorless.

646. Vanadium, Columbium, and Tantalum. — These elements, as previously stated, constitute Sub-group V A and are relatively rare.

Vanadium, V, is more common than columbium and tantalum. It occurs in complex minerals such as *carnotite* (74). The element melts at $1,710^\circ$, and it is multivalent. It forms a variety of compounds, being somewhat analogous to nitrogen. Thus,

V_2O_5 is vanadic anhydride. Other oxides are V_2O , VO , V_2O_3 , and VO_2 . **Ferrovandium**, an alloy, is employed in the manufacture of steel. Most of the vanadium of commerce comes from Peru.

J. W. Marden and M. N. Rich prepared metallic vanadium in 1927.

Columbium, Cb, was discovered by C. Hatchett in 1801, who found it by analyzing some chromium minerals from Connecticut. Hatchett named the mineral "columbite," and the element was called "columbium." It melts at $1,950^\circ$, and has feebly base-forming properties. Columbium is sometimes called "niobium."

Tantalum, Ta, occurs as *ferrous tantalate*, $Fe(TaO_3)_2$, or the mineral *tantalite*. This metal melts at about $2,800^\circ$. Tantalum can be prepared by electrolysis. It has been used in the manufacture of filaments for incandescent lamps, but years ago it was entirely replaced by tungsten. The metal is used in the production of battery chargers and devices for delivering direct current to the plates of radio tubes directly from the lamp socket. It is a weak base-forming element. It resembles platinum in appearance.

Pure metallic tantalum is now produced on a commercial scale. It can be worked cold, drawn, hammered, machined, polished, hardened, rolled, punched, etc. It cannot be soldered, but can be spot-welded to itself and other metals. Its most characteristic chemical property is its unusual resistance to chemical corrosion. It is not attacked by hydrochloric or nitric acid, by aqua regia, nor by dilute sulfuric acid, but appears to be slowly attacked by boiling concentrated sulfuric acid. Solutions of caustic alkalis do not attack tantalum easily. Hydrofluoric acid does attack it, as does also a mixture of hydrofluoric and nitric acids.

Tantalum combines readily with hydrogen, oxygen, or nitrogen, and will take up 740 times its own volume of hydrogen, producing a very coarse-grained, brittle product.

Tantalum has been found especially adaptable for radio electrode and structural parts because of softness and ease in forming, combined with adequate strength and rigidity, and extremely high melting point. In addition, it acts as a gas absorber over the temperature range from red to white heat and becomes a valuable clean-up or "getter" agent, which is particularly important to manufacturers of alternating current radio tubes. It may be readily welded or brazed to such metals as nickel or copper, but as it oxidizes readily in long heating in the air, electric welding is always to be recommended.

EXERCISES

1. Show the relation of the elements of the Arsenic Group to nitrogen and phosphorus.
2. Outline the preparation and properties of the hydrides of the Arsenic Group. Show their relation to ammonia and phosphine.

3. Consult a reference book and note what you can find concerning allotropic forms of arsenic and of antimony.

4. Sketch the preparation and properties of the oxides and acids of arsenic. Compare them with any corresponding compounds of other elements of the Arsenic Group.

5. Describe Marsh's test for arsenic, and tell how arsenic may be distinguished from antimony.

6. Explain the behavior of the following substances in the presence of water: PBr_3 , PBr_5 , AsCl_3 , SbCl_3 , $\text{Bi}(\text{NO}_3)_3$.

7. Compare and contrast the properties of the sulfides of the metals of the Arsenic Group. Are any of them acid anhydrides? Explain.

8. How would you distinguish arsenious acid from arsenic acid, or arsenites from arsenates?

9. According to the old hypothesis of Rose, arsenic acid is reduced by hydrogen sulfide directly to arsenious acid, and the latter then interacts with more hydrogen sulfide to form arsenic trisulfide. Cite evidence to show that this hypothesis is wrong.

10. Compare and contrast the methods employed in preparing arsenic, antimony, and bismuth.

11. Tabulate the chief uses of arsenic, antimony, and bismuth, pointing out any important facts upon which these applications are based.

12. State the law of molecular concentration ("Mass Action") and illustrate it by the action of water on antimony trichloride or bismuth trichloride.

13. Show how a standard solution of arsenious acid may be employed to determine the iodine in a solution of the element.

14. When bismuth trisulfide is treated with hot dilute nitric acid, it dissolves to form bismuth nitrate, nitric oxide, sulfur, and water. Construct the equation for the reaction according to the ion-electron method.

15. How would you prove that the mineral orpiment contains the constituents arsenic and sulfur?

16. Write equations to show the effect of heat upon the following compounds: NaH_2AsO_4 , $\text{Mg}(\text{NH}_4)\text{HAsO}_4$, Na_2HAsO_4 , and H_3AsO_4 .

17. For what are vanadium and tantalum used? State some of their properties.

READINGS AND REFERENCES

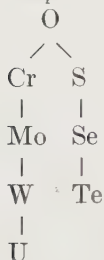
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CHAPTER XXXVI

Group VI



THE CHROMIUM GROUP

647. **Relation to the Sulfur Family and General Characteristics.** — The elements of the Chromium Family are in Group VI of the Periodic System. They are related in a way to the elements of the Sulfur Family, as shown by the accompanying diagram:

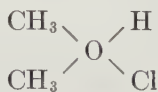
THE CHROMIUM GROUP

Element	Atomic Weight	Atomic Number	Density	Melting Point	Boiling Point
Chromium, Cr. . . .	52.01	24	7.1	1615°	2200°
Molybdenum, Mo. .	96.0	42	9.0	2620°	3700°
Tungsten, W.	184.0	74	19.1	3400°	5900°
Uranium, U.	238.17	92	18.7	1850° (approx.)

The elements of the Chromium Family (Sub-group VI A) form a family of closely related elements. Oxygen may be regarded as linking Sub-group VI A with Sub-group VI B (sulfur, selenium, and tellurium). As seen in a previous chapter, the elements of Sub-group B are acid-forming, but tellurium exhibits some signs of a metallic element.

The elements of Sub-group A are base-producing, or have pronounced metallic properties. These elements when in union with a large proportion of a non-metal such as oxygen possess acidic characteristics. Thus, chromium trioxide (CrO_3) is an acid anhydride.

The elements of Group VI have a multiple valence, the maximum valence being 6: *e.g.*, SF_6 , MoF_6 . Oxygen, however, is nearly always bivalent, but in certain compounds it appears to be quadrivalent, as in



The only really close relationship shown between Sub-group A and Sub-group B is the formation of the acidic trioxides MO_3 .

The elements of the Chromium Group are all characterized by high melting points; therefore, chromium, molybdenum, and tungsten are constituents of special steels, and tungsten is of great importance as filaments in the electric light bulb. They all possess a *variable valence* and show a wide diversity of compounds: *e.g.*, CrCl_2 , CrCl_3 , CrO_3 , Cr_2O_3 , etc.; MoCl_2 , MoCl_3 , MoCl_4 , etc. The higher oxides of these elements are acidic in character:

<i>Anhydride</i>	<i>Acid</i>	<i>Salt</i>
CrO_3	Chromic, H_2CrO_4	Potassium chromate, K_2CrO_4
MoO_3	Molybdic, H_2MoO_4	Ammonium molybdate, $(\text{NH}_4)_2\text{MoO}_4$
WO_3	Tungstic, H_2WO_4	Sodium tungstate, Na_2WO_4

(See SO_3 , H_2SO_4 , and sulfates; also MnO_3 , H_2MnO_4 (manganic acid), and manganates: *e.g.*, K_2MnO_4 .)

When strongly heated, these elements combine with oxygen, with sulfur, and with the halogens. The oxides M_2O_3 are basic in character. These metals do not occur in the free state, but occur as oxides, sulfides, and as salts of the acids H_2MO_4 . They may be prepared by reducing their oxides or chlorides by means of carbon, sodium, aluminium, etc.

CHROMIUM. Cr = 52.01

648. History and Occurrence. — **Chromium** (Greek, *chroma*, meaning color, because all its compounds are colored) was known to exist in the mineral crocoite, PbCrO_4 , as early as 1797 (Vauquelin). Metallic chromium was prepared by Deville in 1857, who reduced the oxide Cr_2O_3 with carbon at a very high temperature. Wöhler obtained it by reducing the chloride with zinc, and then treating the alloy with nitric acid.

Chromium occurs very widely diffused. The metal occurs chiefly in the mineral

Chromite, or chrome iron ore, $\text{Fe}(\text{CrO}_2)_2$ or $\text{FeO} \cdot \text{Cr}_2\text{O}_3$.

Chromite is one of the spinel minerals (589), and is often called ferrous chromite.

The following table, showing the output of chromite just before and at the close of the Great War, is of considerable interest.

PRODUCTION OF CRUDE CHROMITE IN METRIC TONS

	1913	1918
British South Africa.....	63,384	28,000
New Caledonia.....	63,370	26,000
Russia.....	15,000	16,000
Asia Minor.....	14,000	14,000
United States.....	259	84,000
Canada.....		20,000

Before the World War the Western Hemisphere was producing practically no chromite; but by 1918, the production had risen to 132,000 tons, which was possibly 50 per cent of the world's output for that year.

The chief deposits of chromite in the United States are found in California and in Oregon. The total production in the United States in 1919 was over 84,000 tons, of which more than 75 per cent was shipped from California. It is thus seen that the war greatly stimulated the production of chromium.

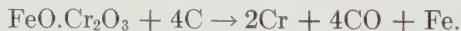
In 1919, there was a decrease of nearly 94 per cent in the shipments of chromite, on account of the ending of the war.

The chrome industry in this country began in Maryland about 1828, and for many years the United States was the leading producer of chromite. After the discovery of large deposits of the ore in Asia Minor, the production declined in the United States, and practically ceased from 1896 to 1900, when the industry was revived to meet the demand for furnace linings.

649. Preparation. — Chromium is readily prepared by reducing chromic oxide by means of aluminium (see "Thermite" Process). The oxide is mixed with finely divided aluminium, a small amount of a "starting mixture" placed on top, and the reduction started by means of burning magnesium. A great quantity of heat is liberated, and a fused mass of chromium is obtained. Following is the equation for the reaction:



The metal may be produced on a large scale by reducing the oxide with carbon in an electric furnace:



The product usually contains from 60 to 70 per cent of chromium, and is used on a large scale in the steel industry.

650. Properties. — In general, the properties of chromium resemble those of iron, but the polished metal is brighter and is somewhat whiter. It has a density of 7.1, a melting point of $1,615^\circ$, while its boiling point is $2,200^\circ$. The metal may be distilled in the electric furnace.

When heated in the oxyhydrogen flame, chromium burns more brilliantly than iron, forming green Cr_2O_3 . Chromium resists

corrosion better than does iron. It dissolves slowly in cold dilute hydrochloric acid, but rapidly in the hot acid, forming chromous chloride, CrCl_2 . The metal also dissolves slowly in dilute sulfuric acid. It is not attacked by concentrated nitric acid, but, like iron, assumes a "passive" state, the reason for which is not clear. The metal also becomes "passive" toward dilute acids after being dipped in a solution of chromic acid. In the electromotive series chromium is placed between zinc and cadmium. Chromium forms important alloys with iron, nickel, cobalt, copper, etc. It also forms amalgams.

Large quantities of the metal are used in the steel industry. **Chrome steel** is extremely hard, dense, and tough, (cutting tools, armor plate, crushers, automobiles, etc.). **Nichrome** is an alloy of nickel, iron, and chromium. It is used extensively for winding the resistances of small electric furnaces; for it has a high resistance, does not oxidize when heated in air, and has a high melting point. **Stellite**, an alloy of cobalt, chromium, and tungsten, is used for high-speed tools and cutlery. **Stainless steel** is used in the manufacture of cutlery. It contains about 12 per cent of chromium and 0.3 per cent of carbon. Chromium also is employed extensively for electroplating metals. Chromium electro-plate appears to resist wear, abrasion, and corrosion remarkably well, and its color is somewhat similar to that of platinum.

651. Chromium Compounds. — Since chromium has a multiple valence and may play the rôle of either a base-forming or an acid-forming element, several classes of chromium compounds are known, depending upon the state of oxidation of the element:

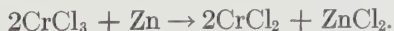
(A) *Chromous Compounds*, in which the element functions as a bivalent metal: *e.g.*, CrO , Cr(OH)_2 , CrCl_2 . Chromous salts may be regarded as derivatives of CrO .

(B) *Chromic Compounds*, in which chromium plays the rôle of a trivalent metal: *e.g.*, Cr_2O_3 , Cr(OH)_3 , CrCl_3 . Chromic compounds may be regarded as derivatives of Cr_2O_3 .

(C) *Compounds in which chromium functions as a sexivalent non-metal*: *e.g.*, CrO_3 , H_2CrO_4 , PbCrO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$. They are derivatives of the anhydride CrO_3 .

(D) *Perchromic Compounds*, in which the element is still more highly oxidized: *e.g.*, perchromic acid and perchromates.

652. Chromous Compounds. — Chromous salts are analogous to ferrous salts, and are usually bright blue in color. They may be prepared by the reduction of chromic salts:



They may also be prepared by dissolving metallic chromium in a dilute acid, such as hydrochloric or sulfuric.

Chromous hydroxide, $\text{Cr}(\text{OH})_2$, and all other chromous compounds are extremely unstable, being readily oxidized to chromic compounds on exposure to air. The compounds are therefore powerful reducing agents.

Chromous acetate, $\text{Cr}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$, may be prepared in the form of deep red crystals; it is insoluble in water, but soluble in hydrochloric acid. This solution, like other chromous solutions, absorbs oxygen readily, being used in gas analysis for determining oxygen in gas mixtures.

The chromous ion, Cr^{++} , is blue, and has a great tendency to pass into the chromic ion.

653. Chromic Compounds. — These compounds contain chromium as a trivalent metal; they are either green or violet in color, and are mostly soluble in water, — the oxide, hydroxide, and phosphate being conspicuous exceptions. Chromic compounds are generally stable, and they are analogous to compounds of aluminium and of ferric iron. As a rule, chromic salts are quite highly hydrolyzed in aqueous solution. The chromic ion, Cr^{+++} , is bluish-violet.

Chromic hydroxide, $\text{Cr}(\text{OH})_3$, may be obtained as a green, amorphous precipitate by treating a solution of a chromic salt with ammonium hydroxide (equation). Several modifications of chromic hydroxide are known, depending upon the state of hydration. The hydroxide is amphoteric, chromites being analogous to aluminates. It is used as a mordant (784).

Ferrous chromite, $\text{Fe}(\text{CrO}_2)_2$, chromite, or chrome iron ore, is the chief source of chromium and chromium compounds. It is a very stable substance and is used as a refractory.

Sodium chromite, NaCrO_2 , appears to be formed when an excess of NaOH is added to a solution of a chromic salt. $\text{Cr}(\text{OH})_3$ is first formed, which either dissolves in an excess of the alkali to form a chromite or forms a colloidal suspension in the alkali solution. By boiling the solution, the hydroxide is reprecipitated.

Chromic oxide, Cr_2O_3 , may be obtained by heating chromic hydroxide; also by the oxidation of the metal. It is very stable and insoluble. It is used as a pigment (green paint and green glass). For this use, it is generally prepared by heating sodium dichromate with such a reducing agent as sulfur:



Cr_2O_3 is analogous to Fe_2O_3 and Al_2O_3 .

Chromic chloride, CrCl_3 , may be prepared by the combined action of chlorine and carbon, or by that of carbon tetrachloride, on Cr_2O_3 at a high temperature:

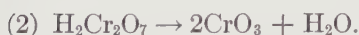
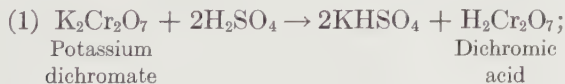


The salt is obtained as brilliant violet-colored, pearly scales. It dissolves with extreme slowness in water, and, on standing, crystals having the formula $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ are deposited. Two forms of this salt are known — a green variety and a violet variety (isomers).

Chromic sulfate, $\text{Cr}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ (see $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$) may be obtained in the form of violet or blue octahedra. When chromic sulfate is crystallized along with the sulfates of the alkali metals, double salts known as alums are formed. Thus, $\text{K}_2\text{SO}_4 \cdot \text{Cr}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ is *chrome-alum*. It is employed extensively in the manufacture of leather. In aqueous solution chromic hydroxide is formed by hydrolysis, and it acts on animal skins very much as does tanbark.

CHROMIC ACID AND ITS DERIVATIVES

654. **Chromic Anhydride**, CrO_3 . — The anhydride of chromic acid may be prepared by treating a cold saturated solution of a dichromate (or chromate) with concentrated sulfuric acid:



The compound separates out in long scarlet needles. It dissolves in water to form **chromic acid**, H_2CrO_4 (or possibly dichromic acid, $\text{H}_2\text{Cr}_2\text{O}_7$). Chromium trioxide is a powerful oxidizing agent, decomposing at 250° to form chromic oxide and oxygen:

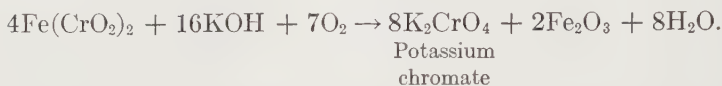


CrO_3 is analogous to SO_3 , and H_2CrO_4 resembles H_2SO_4 , but is unstable.

655. **Chromates**. — *Chromates are analogous to sulfates*, the normal salts of the two acids usually being isomorphous:



When chromite is heated with an alkali (or an alkaline carbonate) in contact with air or an oxidizing agent (*e.g.*, KNO_3), a chromate is formed:

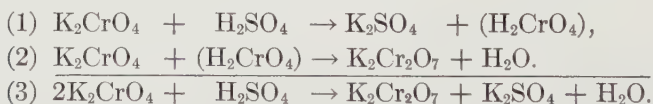


Potassium chromate and the chromates of the other alkali metals are soluble, and the solutions are of a bright yellow color owing to the presence of the chromate-ion, $\text{CrO}_4^{=}$. Potassium chromate is manufactured by heating a mixture of finely divided chromite, potassium carbonate, and lime in contact with air. When Na_2CO_3 is substituted for K_2CO_3 , sodium chromate (Na_2CrO_4) is obtained. The presence of the lime prevents fusion and keeps the mass porous, which facilitates oxidation.

The chromates of potassium and of sodium are used in the manufacture of yellow pigments and dichromates. Chrome yellows have as a basis PbCrO_4 , ZnCrO_4 , or BaCrO_4 . Lead chromate is a brilliant yellow, which mixes well with oil and has great covering power, but is blackened by hydrogen sulfide.

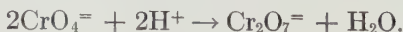
In normal times, in the United States, about 35 per cent of the chromite is used for the manufacture of chemicals, principally dichromates.

656. **Dichromates.** — **Potassium dichromate**, $\text{K}_2\text{Cr}_2\text{O}_7$, is the starting point for the preparation of many compounds of chromium. It is manufactured by treating a saturated solution of potassium chromate with sulfuric acid:



We may regard the chromate and sulfuric acid as first interacting to form unstable chromic acid which interacts with another molecule of K_2CrO_4 to form $\text{K}_2\text{Cr}_2\text{O}_7$. The final result is shown in equation (3). The dichromate crystallizes out, as it is less soluble than potassium sulfate.

From the ionic standpoint, the change of the chromate-ion to the dichromate-ion in the presence of an acid may be explained thus:

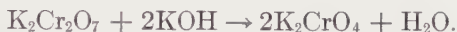


Potassium dichromate forms red trichlinic anhydrous crystals, which melt at 396° . Sodium dichromate, $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$, is cheaper, and is more soluble in water at ordinary temperatures than is the potassium salt. The dichromates are sometimes called **pyrochromates** (see Pyrosulfates, 350).

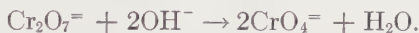
The **dichromate-ion**, $\text{Cr}_2\text{O}_7^{=}$, is of an orange-red color.

657. Chemical Properties of the Dichromates. —

(1) In the presence of solutions of hydroxides of such metals as potassium and sodium, the dichromates are changed into chromates:



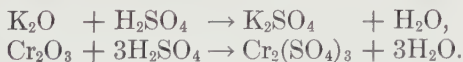
When an orange-red solution of a dichromate is rendered alkaline, it therefore turns yellow. Ionically, the change is as follows:



(2) When a dichromate is treated with concentrated sulfuric acid, chromic anhydride is formed (equation).

(3) Mixtures of dichromates and acids are powerful oxidizing agents. Thus, a mixture of potassium (or sodium) dichromate and strong sulfuric acid is used for cleansing chemical apparatus (glassware).

As an oxidizing agent, a solution of potassium dichromate is frequently used in volumetric analysis to estimate the quantity of a reducing agent such as a ferrous salt. This action of the dichromate may be explained by writing its formula as $\text{K}_2\text{O} \cdot 2\text{CrO}_3$, *i.e.*, the molecule of dichromate is regarded as being equivalent to one molecule of K_2O and two molecules of the anhydride CrO_3 . By treating a solution of potassium dichromate with a reducing agent in the presence of excess acid (*e.g.*, H_2SO_4), we may regard CrO_3 as being reduced to Cr_2O_3 (a metallic oxide), and the latter, as well as K_2O , as interacting with the acid to form sulfates



To illustrate, ferrous sulfate (FeSO_4) may be regarded as $\text{FeO} \cdot \text{SO}_3$. When FeO is oxidized it forms Fe_2O_3 , which interacts with H_2SO_4 to form $\text{Fe}_2(\text{SO}_4)_3$. When an acidified solution of the ferrous salt is treated with a solution of potassium dichromate, the former is oxidized and the latter reduced. One molecule of

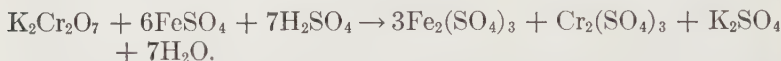
$\text{K}_2\text{Cr}_2\text{O}_7$ contains, for purposes of oxidation, three atoms of oxygen:



One atom of oxygen can oxidize two molecules of FeO to Fe_2O_3 :

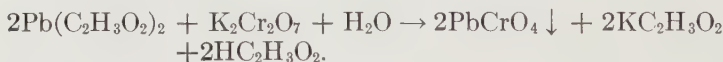


Three atoms of oxygen can therefore oxidize six molecules of the ferrous compound. We may now write the complete equation thus:

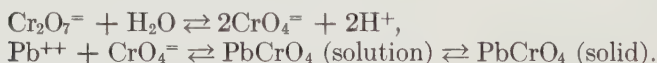


658. Uses of Dichromates. — Dichromates are used in the manufacture of other compounds of chromium (chromates, etc.) as a substitute for tanbark in tanning (chrome tannage, or tawing), and as an oxidizing agent.

When a solution of a lead salt is treated with a dichromate, lead chromate is precipitated:



According to the ionic hypothesis, the dichromate-ion in solution is partly transformed into the chromate-ion, and the latter then interacts with the lead-ion:



In **chrome tannage**, the skins, after appropriate preliminary treatment, are further treated with a solution of potassium (or sodium) dichromate and other chemicals, one of which is a reducing agent. Chromium hydroxide, $\text{Cr}(\text{OH})_3$, is formed by reduction, and is precipitated in the leather. The skin is colloidal and the hydroxide is adsorbed. It is a rapid process, requiring only a few hours. It is employed chiefly for glove leathers, calf skin, and glazed kid.

659. Identification of Chromium. — As chromium compounds are colored, their identification is easy. In analysis, chromium, aluminium, and ferric iron (Fe^{+++}) belong to the same group. They may be precipitated as hydroxides by ammonium hydroxide or sulfide: $\text{Cr}(\text{OH})_3$, $\text{Al}(\text{OH})_3$, and $\text{Fe}(\text{OH})_3$.

The following are some of the tests which may be employed to identify chromium:

(1) Chromium compounds give an emerald-green borax bead (467).

(2) When a chromium compound is fused with sodium carbonate and sodium nitrate, a yellow mass is obtained. Reduction of a chromate yields the green color of a chromic salt.

(3) When a solution of a chromic salt is treated with NH_4OH in the presence of NH_4Cl , a green precipitate of chromic hydroxide is obtained.

(4) When a very concentrated solution of a chromic salt is treated with sodium peroxide, yellow sodium chromate is formed. When a lead salt is added, a yellow precipitate of PbCrO_4 is obtained (see test for Hydrogen Peroxide); it is insoluble in acetic acid.

MOLYBDENUM. $\text{Mo} = 96$

660. **History and Occurrence.** — **Molybdenum**, from a Greek word meaning *lead*, is one of the rarer metals. It most frequently occurs in granite in the mineral



which resembles graphite.

Molybdenum also occurs as lead molybdate, the mineralogical name for which is



The United States and Canada probably have the largest known molybdenum deposits, the former country having been for some years the largest producer of molybdenum ore. Molybdenite also is produced in Australia, Japan, Norway, and Sweden. In 1915 the United States produced 82 tons, and in 1918, 391 tons. In the latter year Australia produced 112 tons and Canada 103 tons. Colorado is now the center of production.

The difference between molybdenite and plumbago was first pointed out by Scheele (1778). Hjelm isolated the metal in 1783.

661. **Preparation, Properties, and Uses.** — Molybdenum may be prepared by the reduction of molybdic oxide, MoO_3 , by the Goldschmidt process; or by reducing the oxide or chloride by hydrogen. **Ferromolybdenum**, an alloy used in the manufacture of special steels, is prepared by treating molybdenite in an electric furnace with coke and iron.

Molybdenum is a metal with silvery luster and has a density of 9 and a melting point of $2,620^{\circ}$. The metal is too volatile for use as a filament in electric lamps, but is used as a support for tungsten filaments. Like iron, it may be tempered and forged, and it takes up carbon. Molybdenum is used in the manufacture of special steels. During the Great War, Germany, being short of tungsten, was forced to substitute molybdenum for tungsten in the manufacture of high-speed tool steels. The metal is added to steel in the form of ferromolybdenum. Tungsten steels are superior. Molybdenum also is employed in the Coolidge X-ray tube.

662. Molybdenum Compounds. — Molybdenum, like chromium, forms many compounds. When molybdenite, MoS_2 , is roasted, **molybdenum trioxide**, MoO_3 , is obtained as a white powder, which turns yellow when heated. It dissolves sparingly in water to form molybdic acid. **Ammonium molybdate**, $(\text{NH}_4)_2\text{MoO}_4$, is formed when MoO_3 is heated with an excess of concentrated ammonia. When a solution of ammonium molybdate is treated with nitric acid and the solution allowed to stand, molybdic acid, $\text{H}_2\text{MoO}_4 \cdot \text{H}_2\text{O}$, in part crystallizes out. When phosphoric acid is treated with a solution of ammonium molybdate in the presence of nitric acid, a yellow precipitate of **ammonium phosphomolybdate**, $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3 \cdot x\text{H}_2\text{O}$, is obtained. Ammonium molybdate is therefore used in the detection and separation of phosphoric acid. The compound also is used in the dyeing of silk. Sodium molybdate, Na_2MoO_4 , is employed in staining leather and for coloring pottery blue. Molybdenum also enters into the composition of a large number of other compounds, such as the following:

(1) Halogen derivatives, — MoCl_2 , MoCl_3 , MoCl_4 , MoCl_5 , MoF_6 , MoOF_4 , MoO_2F_2 , etc.;

(2) Salts in which Mo_2O_3 and MoO_2 play the rôle of basic oxides.

TUNGSTEN. $W = 184.0$

663. Occurrence and Preparation. — **Tungsten** (Swedish, meaning *heavy-stone*) was discovered by Scheele in 1781. The Germans call the element “wolfram.” The chief ore of tungsten is known as

Wolframite, or ferrous-manganese tungstate, $(\text{Fe}, \text{Mn})\text{WO}_4$.
Another important ore, especially in the United States, is
Scheelite, CaWO_4 .

Tungsten occurs almost exclusively in granitic rocks. It is found principally along, or comparatively near, the shores of the Pacific Ocean, the Asiatic shore being richer than the American. Southeastern Asia is the greatest producer of tungsten ores, followed by the United States and Mexico. Until the year 1912, the leading tungsten-producing country was the United States; but in 1913 the ore produced in eastern Asia amounted to about 2,600 metric tons, and in 1918 to more than 18,000, which was more than 57 per cent of the world's production. In 1913 the United States produced about 1,400 metric tons, and the average production from 1916-1918 was over 5,000 tons, the great increase in production being due to the stimulus of the war. After the signing of the Armistice, prices fell rapidly. On account of the abundance of ore and cheap labor, the Chino-Malayan Province is now supplying the greater part of the mineral. Considerable tungsten is also found in South America, especially in Bolivia. In the United States, most of the tungsten ore is produced in California and Colorado, in 1917 each state producing about 2,700 tons of the concentrated ore (carrying 60 per cent of WO_3).

Tungsten may be prepared by roasting the ore to remove arsenic, sulfur, etc., and then heating with sodium carbonate ("soda-ash"). Sodium tungstate is formed, which is dissolved in water, the insoluble impurities being left behind. The salt is purified by recrystallization, the hydrate $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ being obtained. When the solution of salt is acidulated, free tungstic acid, $\text{H}_2\text{WO}_4 \cdot \text{H}_2\text{O}$, is obtained, which, on ignition, yields tungstic anhydride, WO_3 . The metal may be obtained by reducing this oxide with carbon in a furnace, a solid powder being obtained. WO_3 may also be reduced by the thermite process; also by means of hydrogen in an electrically heated furnace.

Ferro-tungsten, an alloy of tungsten and iron, is produced by direct reduction from wolframite containing a low percentage of manganese.

664. Properties and Uses. — Tungsten is a steel-gray, very hard metal, which has a density of about 19. Its melting point is about $3,400^\circ$, which is higher than that of any other metal. The temperature of the electric furnace is required for melting and vaporizing the metal. Carbon is the only element having a higher melting point than tungsten, but the latter has a lower vapor pressure. When tungsten is obtained by reduction, it is in the form of a powder; for the temperature is not high enough to fuse the metal. It can be welded by hammering, and drawn out into very fine filaments. The ductile metal may be obtained by pressing the powder into bars or rods, which are heated by means of electric furnaces and then worked up in a swaging machine into smaller rods. By repeating the process, the metal becomes stronger and

more malleable and the rods smaller and smaller. It may be fashioned into sheets by rolling or hammering, or into wire by drawing the small rods through diamond dies until fine enough for electric light filaments. The final filament has greater tensile strength than that of all other metals. When the metal is hammered and drawn, therefore, its tensile strength is greatly increased.

Tungsten does not rust and is not attacked by nitric, hydrochloric, or sulfuric acid; it dissolves very readily, however, in a mixture of nitric and hydrofluoric acids. At high temperatures, it combines with oxygen and with nitrogen.

Tungsten is used extensively in the manufacture of *high-speed tool steel*. As the tools can be heated to redness without losing their temper, the efficiency of the workmen is greatly increased. No highly satisfactory substitute for tungsten has been found, but molybdenum is used to a certain extent. Tungsten is a constituent of *stellite*. The metal also is used largely in the manufacture of filaments for incandescent lamps. The bulbs are either exhausted or filled with argon (why?). This lamp is far more efficient than the one containing the ordinary carbon filament, 1.30 watts per candle power being required for the former while 3.25 watts are required for the latter. Tungsten also is used for targets and cathodes of X-ray tubes, for electric contacts in explosion engines, in special alloys, in mordants, and in minor chemicals.

665. Tungsten Compounds. — We have seen that tungsten compounds are similar to those of molybdenum. **Sodium tungstate**, Na_2WO_4 , is used in fire-proofing fabrics and as a mordant in dyeing. Certain tungsten compounds are valuable pigments. **Phosphotungstic acid**, $\text{H}_3\text{PO}_4 \cdot 12\text{WO}_3 \cdot 18\text{H}_2\text{O}$, is analogous to phosphomolybdic acid; it is used as a reagent in detecting certain alkaloids.

URANIUM. $U = 238.17$

666. History and Occurrence. — Uranium was discovered in the mineral pitchblende by Klaproth in 1789, and he named the metal uranium in honor of Herschel's discovery of the planet *Uranus*, in the year 1781. Uranium is not a very abundant element; it is found in

Pitchblende or uraninite, U_3O_8 ,

or in secondary minerals derived therefrom. Pitchblende contains from 40 to 90 per cent of U_3O_8 . Uranium occurs in fair

abundance in

Carnotite, $K_2O \cdot 2UO_3 \cdot V_2O_5 \cdot 3H_2O$,

which is a yellow mineral found in Colorado and in Utah. It is a uranate and vanadate of potassium. While Klaproth discovered the presence of uranium in uraninite in 1789, the metal was not obtained in the pure state until the year 1842. This was accomplished by Peligot, who obtained it by reducing the tetrachloride by means of sodium or potassium. The metal can be prepared by heating U_3O_8 with sugar charcoal in an electric furnace.

667. Properties and Uses. — Uranium is a white metal with a density of 18.7 and a melting point of about $1,850^\circ$. It undergoes slow oxidation in the air, dissolves in ordinary acids to form salts, decomposes water, and unites with chlorine, sulfur, and nitrogen. Uranium is both a base-forming and an acid-forming element, as is chromium. It forms a great variety of compounds. Uranium has the heaviest atom of all the elements. It is interesting to recall that its atom breaks down spontaneously, giving rise to other elements, such as radium and helium (see the Radioactive Elements, Chap. IV). The best known salts of uranium are those containing the uranyl radical (UO_2), in which the radical plays the rôle of a bivalent metal; *e.g.*, uranyl nitrate, $(UO_2)(NO_3)_2 \cdot 6H_2O$, and uranyl sulfate, $(UO_2)SO_4 \cdot 3H_2O$. These are beautiful yellow salts. The dioxide UO_2 is basic, and UO_3 is uranic anhydride. U_3O_8 is the most stable of its oxides.

Compounds of uranium are used to impart a yellowish-green fluorescence to glass, as well as in China painting to produce a velvety black color. *Most of the uranyl salts are strongly fluorescent.*

EXERCISES

1. Give the names and symbols of all the elements in Group VI of the Periodic Table. Enumerate the chief characteristics of the elements of the chromium family, and show their relation to the sulfur family.

2. How does chromium occur? What was the influence of the late war upon the production of the element? Why is chromite termed one of the spinel minerals? What is its relation to magnetite?

3. Outline the preparation of metallic chromium and ferrochromium. What are the properties of chromium? What is meant by the "passive" state of a metal? Mention the chief uses of chromium.

4. Point out just how the element chromium may play the rôle of a bivalent and a trivalent metal, as well as that of a sexivalent non-metallic element. Illustrate fully.

5. Explain fully, including equations, how you would —

- (1) Obtain CrCl_2 from CrCl_3 ;
- (2) Prepare $\text{Cr}(\text{OH})_3$ from chrome alum;
- (3) Prepare chrome alum from $\text{Cr}(\text{OH})_3$;
- (4) Prepare potassium chromate from chromite;
- (5) Transpose potassium chromate into the dichromate;
- (6) Prepare chromic anhydride; and
- (7) Prepare lead chromate from sodium dichromate

6. Using the ion-electron method, write chemical equations to show (1) the interaction of potassium dichromate and a ferrous salt in the presence of sulfuric acid; (2) the interaction of a dichromate and concentrated hydrochloric acid.

7. When a solution of chromic sulfate is treated with a limited amount of a solution of potassium hydroxide, a green precipitate is formed, which dissolves to form a green solution upon adding the hydroxide in excess. Explain. When an excess of chlorine is passed into the green solution, it turns yellow. Explain.

8. When a solution of a chromic salt is treated with ammonium sulfide, chromic hydroxide is formed. Explain.

9. Outline the occurrence, preparation, properties, and uses of molybdenum. Show the relation of the element to chromium.

10. How may the mineral molybdenite be converted into molybdic anhydride, and the latter into ammonium molybdate? For what is the molybdate used?

11. Give the occurrence of tungsten. Where are the chief deposits of tungsten minerals found? Outline the preparation of metallic tungsten. What are its properties and uses?

12. Explain how sodium tungstate may be prepared from wolframite, and tungstic acid and its anhydride obtained from a tungstate.

13. A tungsten electric filament was dissolved in nitric and hydrofluoric acids and the solution evaporated to dryness and the residue ignited. What was left? The residue was then fused with soda-ash. What was formed? The product was dissolved in water and then acidified, whereupon a white precipitate was obtained. Explain. State how metallic tungsten could be obtained from the precipitate.

14. Explain as fully as you can the changes which occur when tungsten powder is converted into electric light filaments. Why are the filaments drawn out until they are so small?

15. From an economic standpoint, what is the significance of the fact that the tungsten filament requires 1.30 watts per candle power, while the ordinary carbon filament requires 3.25 watts?

16. Outline the occurrence and the preparation of uranium. What does the fact signify that radium and helium are always associated with uranium ores? What are pitchblende and carnotite?

17. What are the properties of uranium? Write the formulas of two uranyl salts. Mention two uses of uranium compounds.

READINGS AND REFERENCES

- EVANS. Metals and Metallic Compounds, Vol. II, pp. 301-361.
 LOWRY. Inorganic Chemistry, Chap. XXXIX.
 WYSOR. Metallurgy.

CHAPTER XXXVII

MANGANESE. $Mn = 54.93$

668. **Relations of the Element.** — Manganese is found in Group VII of the Periodic System. The halogens also belong to this group, but in most respects they do not resemble manganese. Thus, manganese, like chromium, plays the rôle of both a metal and non-metal. Unlike the halogens, it is never univalent. Manganese resembles chromium and iron much more closely than it does the halogens, but Mn_2O_7 and Cl_2O_7 are similar, as are $HMnO_4$ (permanganic acid) and $HClO_4$. Like chromium, manganese forms the basic oxides RO and R_2O_3 ; a dioxide, RO_2 ; and an anhydride, RO_3 . The element resembles iron in forming oxides of the type RO , R_2O_3 , and R_3O_4 ; and ferrous and ferric salts are analogous to chromous and chromic salts. In manganous salts (*e.g.*, $MnSO_4$) manganese is bivalent, while it is trivalent in manganic salts.

We have seen that the halogens form a closely related family (266).

It should be noted that the German scientist Noddack announced the discovery of two missing elements in the spring of 1925. They were discovered by X-ray analysis, and were named *masurium* and *rhenium*. Their atomic numbers are 43 and 75 respectively, and they are classed with manganese.

669. **Occurrence.** — **Manganese** (probably from Latin *magnes*, because of its resemblance to the magnet) was first isolated by Gahn in 1774.

Manganese is never found native, but in combination it occurs widely diffused in small quantities. It occurs most commonly as silicates, oxides, and carbonates, its chief mineral being the dioxide —

Pyrolusite MnO_2 .

The color and streak of pyrolusite are black.

Other manganese minerals are

Braunite Mn_2O_3 (or $MnMnO_3$) and
Hausmannite Mn_3O_4 .

To show the influence of war upon the production and use of manganese compounds, the following table is of interest.

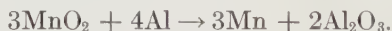
MANGANESE ORE, IN METRIC TONS, PRODUCED BY LEADING COUNTRIES
FOR THE YEARS 1913 AND 1918

	1913	1918
Russia.....	1,310,000
India.....	828,000	526,000
Brazil.....	122,000	351,000
United States.....	2,700	311,000
Cuba.....	84,000
Spain.....	21,600	77,700

From 1910 to 1913, Russia, India, and Brazil supplied about 95 per cent of the world's production. Before the war, the United States imported most of the manganese ore and manganese alloys required in our industries. The war showed that domestic ores could supply about 35 per cent of the Nation's needs. The signing of the Armistice brought a sudden collapse to the mining of manganese ores in the United States. A great deal of the American ore is of inferior quality.

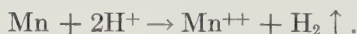
Manganese is absorbed in limited amounts by growing plants.

670. **Preparation.** — Pure metallic manganese is best obtained by reducing MnO_2 by the Goldschmidt process:



The temperature rises to about $3,000^\circ$. Large quantities of alloys of iron and manganese are produced by reducing a mixture of ores of iron and manganese by means of carbon in the blast furnace. When MnO_2 is reduced by carbon, the metal always contains carbon.

671. **Properties.** — Manganese is a gray or reddish-white metal, having the appearance of cast iron. It is hard and brittle, has a density of approximately 8, melts at $1,230^\circ$, and boils at about $1,900^\circ$. Manganese has the lowest melting point of any steel-forming metal. The presence of carbon greatly increases the hardness of manganese. The metal oxidizes quite readily in the air and dissolves in dilute acids to form salts and hydrogen:



In the electromotive series manganese is between aluminium and zinc. Above $1,210^\circ$, it combines rapidly with nitrogen. In its chemical deportment manganese most closely resembles iron.

672. **Uses.** — Manganese is used on a large scale in the manufacture of steel; it increases the toughness of the steel, and acts as a deoxidizer, as well as a medium for the introduction of the requisite amount of carbon. It is added to steel in the form of alloys — **ferromanganese** (usually about 80 per cent of Mn) and **spiegeleisen** (20 per cent or less of Mn). On the average, about 14 pounds of manganese are required to produce a ton of steel. **Manganese bronze**, an alloy of copper, zinc, manganese and other metals, resists corrosion; it is used for propeller blades. **Manganin**, an alloy of copper, nickel, and manganese, is employed as standard resistance wire in electrical measurements. In the year 1917, 25,000 tons of high-grade manganese ore (pyrolusite) were used in the manufacture of dry batteries.

COMPOUNDS OF MANGANESE

673. **Classes of Compounds.** — As manganese has a multiple valence (2, 3, 4, 6, or 7) and is capable of playing the rôle either of a base-forming or of an acid-forming element, it takes part in the formation of several classes of compounds:

(1) *Manganous compounds.* These may be regarded as derivatives of MnO or Mn(OH)_2 : e.g., MnCl_2 , MnSO_4 , etc. These salts have a pale-pink color. They are analogous to salts of magnesium and of ferrous iron.

(2) *Manganic compounds.* Derivatives of Mn_2O_3 or Mn(OH)_3 : e.g., $\text{Mn(NO}_3)_3$, $\text{Mn}_2(\text{SO}_4)_3$. These salts are similar to those of ferric iron and of aluminium, but are very unstable. They have a violet color.

(3) *Manganites.* They may be regarded as derivatives of the oxide MnO_2 : e.g., H_2MnO_3 , CaMnO_3 (calcium manganite).

(4) *Manganates.* We may look upon these as being derivatives of the anhydride MnO_3 , just as sulfates are derivatives of SO_3 or H_2SO_4 : e.g., H_2MnO_4 , Na_2MnO_4 . These salts have a green color, and hydrolyze much more readily than do sulfates and chromates.

(5) *Permanganates.* Derivatives of the anhydride Mn_2O_7 : e.g., HMnO_4 and KMnO_4 (potassium permanganate). They are analogous to perchlorates. These compounds possess a reddish-purple color, and are very powerful oxidizing agents.

674. **Oxides of Manganese.** — Manganese forms six well-defined oxides, as shown in the table below.

OXIDES OF MANGANESE

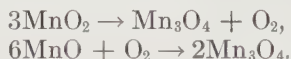
<i>Compound</i>	<i>Formula</i>	<i>Character of Oxide</i>
Manganous oxide	MnO	Strongly basic
Manganic oxide	Mn ₂ O ₃	Weakly basic
Manganese dioxide	MnO ₂	Feebly acidic
Manganese trioxide	MnO ₃	Manganic anhydride
Manganese heptoxide	Mn ₂ O ₇	Permanganic anhydride
Manganese tetroxide (Mangano-manganic oxide)	Mn ₃ O ₄	Stable neutral oxide; probably a salt

Manganous oxide, MnO, may be obtained by igniting the higher oxides or the carbonate in a current of hydrogen.

Manganic oxide, Mn₂O₃, occurs as the mineral braunite.

Manganese dioxide, MnO₂, occurs abundantly as the mineral pyrolusite. It is an active oxidizing agent, and is used in the preparation of oxygen, chlorine, dry batteries, as a source of manganese, for drying black paints, and to remove the green color of glass (due to compounds of iron), yellow ferric compounds being formed, which are masked by the violet manganese silicates which are also formed. MnO₂ is formed at the anode when salts of manganese are subjected to electrolysis.

Manganese tetroxide, Mn₃O₄, may be produced by strongly heating any of the other oxides of manganese in the presence of air:



675. Manganous Compounds. — Manganous salts may be formed by dissolving the basic oxide MnO in acids.

Manganous chloride separates from water solution as the pink hydrate, MnCl₂·4H₂O. The salt is deliquescent, and is used in dyeing.

Manganous sulfate, MnSO₄·7H₂O, separates from water in the form of pink crystals.

Manganous sulfide, MnS, a flesh-colored compound, is formed by treating a solution of a manganous salt with an alkali sulfide. The precipitate is hydrated. The anhydrous compound is green. The salt is soluble even in acetic acid.

The manganese-ion, Mn⁺⁺, has a pale pink color and no special physiological action. It resembles the magnesium-ion in many respects.

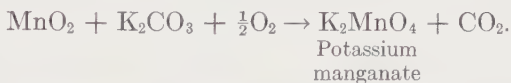
Unlike ferrous salts, soluble manganous salts do not oxidize in the air in the presence of strong acids.

Manganous salts are far more important than manganic salts.

The latter are more completely hydrolyzed than are ferric salts. Manganic salts are also unstable: *e.g.*, manganic chloride, MnCl_3 , readily breaks down into manganous chloride and chlorine.

676. Manganites and Manganates. — **Manganites** may be obtained by fusing alkalis with the acid anhydride MnO_2 , just as silicates are formed by the interaction of alkalis and SiO_2 . They are considered to be salts of manganous acid (H_2MnO_3): *e.g.*, CaMnO_3 ($=\text{CaO}.\text{MnO}_2$) is calcium manganite. As a rule, these salts have a variable composition and are rather complex.

Manganates may be formed by fusing a manganese compound with caustic alkali (or an alkali carbonate) in the air, or in the presence of an oxidizing agent such as KNO_3 :

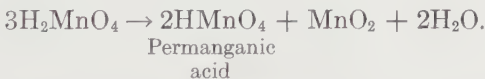


Manganates are green in color, and are regarded as derivatives of manganic acid, H_2MnO_4 . They are analogous to sulfates and chromates. Free manganic acid has never been obtained, and its salts are unstable in the presence of water (hydrolysis) or of acids, even carbonic and acetic. Thus, when CO_2 is passed through a solution of K_2MnO_4 , potassium permanganate (KMnO_4) is formed:



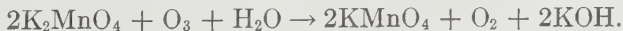
The solution changes from green to purple-red.

Manganic acid is unstable:



In this change two-thirds of the manganese is oxidized to HMnO_4 and one-third is reduced to MnO_2 . Manganates are only stable in excess of free alkali.

677. Permanganates. — Manganese dioxide or pyrolusite, MnO_2 , is used in the preparation of permanganates. In the previous article we saw how MnO_2 may be oxidized to potassium manganate (K_2MnO_4) and how the latter may be converted into permanganate. Formerly, this process was employed in the manufacture of **potassium permanganate**; but as one-third of the manganese is transformed into MnO_2 , the salt is now manufactured by oxidizing a solution of K_2MnO_4 with ozone:



Potassium permanganate forms purple crystals with a greenish luster, which are isomorphous with potassium perchlorate, KClO_4 . The salt is readily soluble in water, forming a deep purple-colored solution, due to the permanganate-ion, MnO_4^- . It is a powerful oxidizing agent and is largely used as such. Thus, glycerine may be ignited by mixing finely divided KMnO_4 with the liquid.

Sodium permanganate, NaMnO_4 , is similar to potassium permanganate, but it is too soluble to be readily obtained by crystallization.

Some of the uses of permanganates have already been mentioned. "Condy's disinfecting fluid" contains aluminium permanganate. The salt hydrolyzes, forming permanganic acid.

When **barium permanganate**, $\text{Ba}(\text{MnO}_4)_2$, is treated with dilute sulfuric acid, permanganic acid, HMnO_4 , is formed (equation). The acid is very unstable, being a powerful oxidizing agent.

When pure KMnO_4 is gradually added to well-cooled concentrated sulfuric acid, the salt dissolves, forming an olive-green solution. By cooling the solution and carefully adding water, **manganese heptoxide**, Mn_2O_7 , separates out as a reddish-brown oily liquid; it is very unstable, a powerful oxidizing agent, and is the anhydride of permanganic acid:



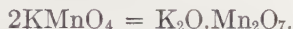
Manganese heptoxide is explosive, and it ignites paper and other organic substances (see HClO_4 and Cl_2O_7).

678. Potassium Permanganate as an Oxidizing Agent.—Potassium permanganate is employed extensively as an oxidizing agent, both industrially and in the laboratory. Thus, it is a valuable disinfectant, a bleaching agent, colors wood brown, and is of great service in volumetric analysis for the determination of reducing agents, such as ferrous salts and oxalic acid. In analysis no indicator is required, for the solution is purple, and when the permanganate is reduced the solution loses its color, and when it is in slight excess the solution is colored.

The action of potassium permanganate as an oxidizing agent depends upon the nature of the reducing agents, as well as upon whether the reactions are carried out in acid solution or in alkaline or neutral solution.

In permanganates, manganese has a valence of +7, and when permanganates are reduced in the presence of acids, the valence of manganese changes to +2, which means that a manganous salt is formed.

Looked at from another standpoint, we may regard two molecules of KMnO_4 as containing potentially one molecule of K_2O and one of the anhydride, Mn_2O_7 :



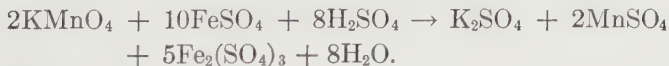
Now, Mn_2O_7 is capable of yielding 2MnO and 5O , *i.e.*, five available oxygen atoms, which, in the presence of an acid, *e.g.*, H_2SO_4 , are free to oxidize a reducing agent (*e.g.*, FeSO_4). Furthermore, let us regard a molecule of FeSO_4 as being equivalent to $\text{FeO} \cdot \text{SO}_3$. One atom of oxygen is required to oxidize 2FeO to Fe_2O_3 :

$2\text{FeO} + \frac{1}{2}\text{O}_2 \rightarrow \text{Fe}_2\text{O}_3$; therefore, 5 atoms of oxygen can oxidize 10FeO ($=10\text{FeSO}_4$) to the ferric state.

Let us furthermore consider that the metallic oxides (K_2O and MnO) interact with H_2SO_4 to form sulfates. We may now write:

- (1) $\text{K}_2\text{O} + \text{H}_2\text{SO}_4 \rightarrow \text{K}_2\text{SO}_4 + \text{H}_2\text{O}$,
- (2) $2\text{MnO} + 2\text{H}_2\text{SO}_4 \rightarrow 2\text{MnSO}_4 + 2\text{H}_2\text{O}$,
- (3) $10\text{FeSO}_4 + 5\text{H}_2\text{SO}_4 + 5\text{O} \rightarrow 5\text{Fe}_2(\text{SO}_4)_3 + 5\text{H}_2\text{O}$.

The complete equation for the reaction when a solution of ferrous sulfate is treated with a solution of permanganate in the presence of an excess of sulfuric acid may now be written thus:



The hydrogen of the acid is oxidized to water.

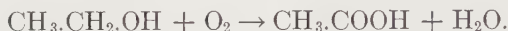
When KMnO_4 plays the rôle of an oxidizing agent in alkaline or neutral solution, we may regard the Mn (valence +7) as being reduced to the quadrivalent state (valence +4). The permanganate is reduced to MnO_2 or to $\text{MnO}_2 \cdot x\text{H}_2\text{O}$. In the presence of the alkali the permanganate is first converted into manganate (green), which loses oxygen, forming the hydrated dioxide:

- (1) $2\text{KMnO}_4 + 2\text{KOH} \rightarrow 2\text{K}_2\text{MnO}_4 + \text{H}_2\text{O} + (\text{O})$; and
- (2) $2\text{K}_2\text{MnO}_4 + 2\text{H}_2\text{O} \rightarrow 2\text{MnO}_2 + 4\text{KOH} + \text{O}_2$.

This may be readily shown by adding finely divided zinc to an alkaline solution of KMnO_4 .

Two molecules of KMnO_4 therefore contain three atoms of "available" oxygen.

To illustrate, when a dilute alkaline solution of KMnO_4 is added to ethyl alcohol, $\text{CH}_3\text{CH}_2\text{OH}$, the latter is oxidized to acetic acid:



Four molecules of KMnO_4 yield six atoms of oxygen, which can oxidize three molecules of alcohol to acetic acid (equation).

All the metals, from the very active ones, such as magnesium and zinc, through the noble metals, reduce dilute neutral solutions of KMnO_4 . Thus, when mercury is shaken with a dilute solution of permanganate, the metal is quickly oxidized and the permanganate reduced. Moreover, the solution contains KOH , for it has an alkaline reaction. A black precipitate of hydrated manganese dioxide also appears. Again, finely divided platinum or gold will very slowly reduce the permanganate solution. In general, we may regard the potassium permanganate, in the presence of the reducing agent, as interacting with water thus:



679. Detection of Manganese. — The following tests enable one to detect the presence of manganese:

(1) When a solution of a manganous salt is treated with ammonium sulfide, a flesh-colored precipitate of the hydrated sulfide, $\text{MnS} \cdot x\text{H}_2\text{O}$, is formed; it is soluble in acetic acid.

(2) When a substance containing manganese is heated on platinum foil in the presence of an alkali and KNO_3 , a green manganate is formed.

(3) When a small amount of a manganese compound is heated in a bead of borax or of salt of phosphorus, the bead is colored amethyst red in the oxidizing flame; but when heated in the reducing flame, the bead becomes colorless.

(4) If a solution containing only traces of manganese is boiled with silver nitrate, ammonium persulfate, and nitric acid, purple-red permanganic acid is formed. This is an extremely delicate test.

EXERCISES

1. To which group of the Periodic System does manganese belong? Outline its chemical relations.

2. Give the occurrence and preparation of manganese. Discuss the relation of the element to the World War. Where are the chief deposits of manganese ores found in this country?

3. State the physical and chemical properties of manganese. What are its chief uses? Mention its chief alloys, giving their composition.

4. Name five different classes of compounds in which manganese is found and point out the valence of the element in each case.

5. Give the names and formulae of five oxides of manganese, and state the chief characteristic of each.

6. How would you prepare the following oxides: MnO , MnO_2 , Mn_3O_4 , and Mn_2O_3 ? Which of these compounds is the most important? Why?

7. Write chemical equations to show (1) what is formed when MnO_2 is strongly heated; (2) its interaction with concentrated hydrochloric acid; and (3) what occurs when it is heated with concentrated sulfuric acid.

8. Explain how you would prepare any manganous salt. Compare manganous salts with those of magnesium and of ferrous iron. Mention one way in which manganous salts differ from ferrous salts. How would you identify the manganous ion, Mn^{++} ?

9. Explain why manganites are regarded as derivatives of MnO_2 .

10. Show, including equation, how to convert MnO_2 into sodium manganate. State a characteristic property of manganates.

11. When a solution of potassium manganate is treated with CO_2 , a purple-red solution is obtained. Explain.

12. Starting with pyrolusite, outline a good method for preparing KMnO_4 . State the properties and uses of the salt.

13. Write chemical equations to show the following: (1) The oxidizing action of KMnO_4 in acid solution; (2) the oxidizing action of KMnO_4 in alkaline or neutral solution. First write the molecular equations, and then write them by the ion-electron method.

14. When a solution of KMnO_4 is treated with H_2O_2 in the presence of H_2SO_4 , the permanganate loses its color. Explain, including the equation for the reaction.

15. Show that a normal solution of potassium permanganate contains 31.606 g. of the salt per liter. Show that 0.7 g. of Mohr's salt, $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$, contains approximately 0.1 g. of ferrous iron.

16. 0.521 g. of Mohr's salt, $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$, is dissolved in pure water, acidulated with sulfuric acid, and then oxidized by a tenth normal solution of potassium permanganate. What volume of the solution is required, and what weight of permanganate does it contain?

17. How much iodine could be liberated from an iodide by the chlorine obtained by treating 5 g. of pyrolusite containing 90 per cent of MnO_2 , with an excess of hydrochloric acid?

18. 1.05 g. of impure pyrolusite was treated with hydrochloric acid and the chlorine passed into an excess of sodium iodide. The liberated iodine required for decolorization 200 cc. of a solution of arsenious acid that had been made equivalent to $N/10$ iodine solution. What per cent of manganese dioxide did the pyrolusite contain?

19. Cite experimental evidence to show that manganese is fairly electro-positive in character.

20. How does the character of manganese change with change in valence? What is the relation of the valence of an atom to the number of electrons gained or lost? Illustrate in case of the element manganese. Do the chemical properties of an element depend more upon the electrical constitution of its atom than upon the atomic weight? Give reasons for your answer.

READINGS AND REFERENCES

EVANS. Metals and Metallic Compounds, Vol. II, pp. 362-383.

MELLOR. Modern Inorganic Chemistry, Chap. XXV.

CHAPTER XXXVIII

IRON, COBALT, AND NICKEL

680. **Relationships and General Characteristics.** — Iron, cobalt, and nickel belong to Group VIII of the Periodic Table. In the first long period of this table, the two sets of analogues to the elements of the short periods are linked by iron, cobalt, and nickel; therefore, these metals have long been known as “transitional elements.” The eighth group is unique in that it possesses three families of elements each of which contains three elements.

The elements of the iron family follow in series chromium and manganese, possess similar properties, and have atomic weights which are very nearly of the same value, as may be seen in the table below.

Element	Atomic Weight	Atomic Number	Density	Melting Point	Boiling Point	Oxides
Iron (<i>ferrum</i>), Fe	55.84	26	7.86	1530°	3000°	FeO, Fe ₂ O ₃ , Fe ₃ O ₄
Cobalt, Co.....	58.94	27	8.7	1480°	2900°	CoO, Co ₂ O ₃
Nickel, Ni.....	58.69	28	8.7	1452°	2900°	NiO, Ni ₂ O ₃

According to the periodic law, nickel should follow iron, but the chemical properties of cobalt place it next to iron. Their atomic numbers are Fe 26, Co 27, and Ni 28, which places them in the proper order. It is interesting to recall that chromium has the atomic number 24, while that of manganese is 25.

Cobalt and nickel resemble one another very closely; indeed, much more closely than they resemble iron, which resembles manganese and chromium.

In general, it may be stated: The elements are difficult to melt, iron being the least fusible and nickel the most fusible. The metals are magnetic, iron showing this property most strongly. Iron forms the most stable oxides and chlorides, and nickel the least stable. Thus, FeCl₃ can be volatilized without decomposition, while CoCl₃ is very unstable, and NiCl₃ is unknown. Iron forms ferrous and ferric salts; cobalt, cobaltous and cobaltic salts;

but *nickel forms nickelous salts only*. Iron forms ferrates, M_2FeO_4 , which resemble manganates and chromates.

All the metals occlude hydrogen, nickel being superior in this respect. In the finely divided state they are employed as catalysts. Thus, nickel is used in the hydrogenation of fats and unsaturated hydrocarbons.

Iron rusts when exposed to moist air, but cobalt and nickel undergo oxidation only when heated in air. All these metals form carbonyls of the type $M(CO)_4$.

 Iron. Fe = 55.84

681. Historical. — Archaeologists divide prehistoric time into three periods, namely, the Stone, Bronze, and Iron Ages. The Bronze Age began in Greece about 5,000 years ago, and the Iron Age began about 800 years later, or about 2,300 B.C. In Egypt, Chaldea, Assyria, and China the age of iron perhaps reaches as far back as 4,000 years before the Christian era. Pieces of iron of great antiquity have been found, an iron implement having been discovered in an Egyptian pyramid. It is certain, then, that iron implements were employed in the ancient world; indeed, the old symbol for the metal was that representing the spear and shield of Mars, the god of war, — ♂.

Great skill in metallurgy was attained at an early period by the Hindus, iron being one of the six metals which are mentioned in their ancient literature. Their extraordinary skill in the metallurgy of iron is well illustrated in the celebrated iron pillar near Delhi, which was manufactured about 1,500 years ago.

682. Occurrence. — Iron occurs very abundantly and widely distributed, constituting 4.5 per cent of the earth's crust, which places it next to aluminium amongst the metals. Iron in the free state has been found in considerable masses in Greenland. The occurrence of the metal in large lumps may have been due to the firing of coal-pits; or it may possibly have been of meteoric origin. Iron is assimilated by plants and animals. It is an essential constituent of hemoglobin and therefore plays a very important part in life-processes. Without sufficient iron in the soil a plant becomes pale, while a deficiency of iron in the blood is indicated by the pallor of the cheeks. When the portion of iron in the blood is reduced too low, our bodies are attacked by disease-producing germs. It is now customary to have laboratories where the number of iron-bearing corpuscles in the blood may be counted.

Iron in the combined state occurs in many minerals and in most rocks and in the soil.

The four important ores of iron are as follows:

Hematite (red hematite).....	Fe_2O_3
Limonite (brown hematite).....	$2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$
Magnetite.....	Fe_3O_4
Siderite.....	FeCO_3 .

Hematite is by far the most important iron ore in the United States. In 1918 it constituted nearly 95 per cent of the iron ore mined, limonite and magnetite constituting the other 5 per cent. The pure mineral contains 70 per cent of iron.

Limonite is the chief ore of France and of Germany, and is also abundant in the southern part of the United States. Pure limonite contains 59.9 per cent of iron.

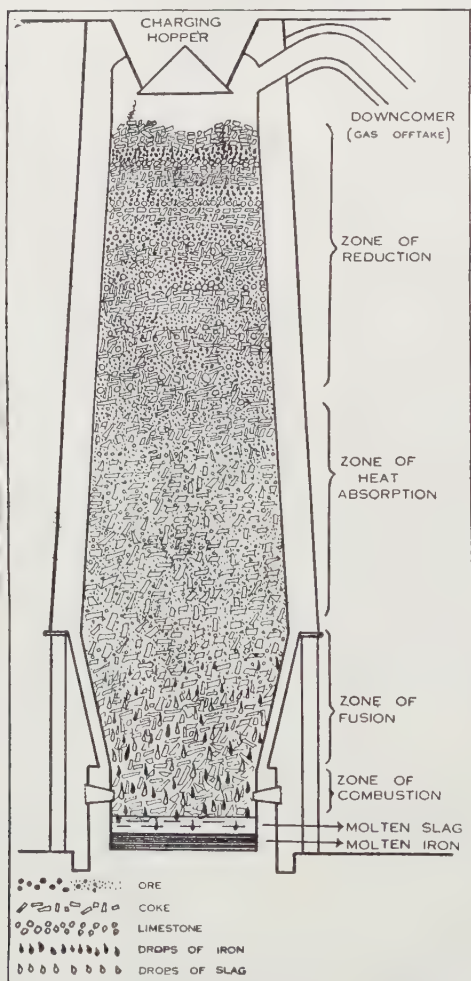
Magnetite constitutes the richest of the iron ores (72.4 per cent of Fe). It is abundant in Norway and Sweden and is mined on a considerable scale in New York, Pennsylvania, and New Jersey. The most important English ore of iron is **clay iron-stone** or **argillaceous iron ore**; it is a spathic iron ore, found associated with clays and shales of the coal-measures. The "black band" iron-stone contains from 20 to 25 per cent of carbonaceous matter.

Iron pyrites, FeS_2 , is very abundant, but is not well adapted to the production of iron, owing to its high content of sulfur.

The number of gross tons of iron ore shipped from our mines in 1918 was 72,000,000, valued at \$244,000,000. Of the total, Minnesota furnished 43,260,000 tons, Michigan 17,580,000, Alabama 6,120,000 and Wisconsin 1,168,000.

683. Metallurgy of Iron. — Iron on the commercial scale is produced by first calcining the ore, if necessary, and then subjecting it to the operation of smelting in huge blast furnaces, limestone usually being used as the flux and coke as the reducing agent (Fig. 191). Furnaces are generally located so as to secure as cheap a supply as possible of the three great raw materials required in the manufacture of pig iron. By the calcination of the ore, carbonates yield oxides of iron and carbon dioxide; hydrated oxides give up water; and sulfides are oxidized. The oxides of iron, limestone, and coke are raised to the top of the furnace by means of a hoist. The furnace is usually 90 to 100 feet in height, and its diameter ranges from 12 to 20 feet. A furnace 90 feet in height and 12 to 14 feet in diameter normally produces 500 to 600 tons of pig iron in 24 hours. The furnace is constructed of heavy

steel plates and lined with fire-brick. The raw materials are introduced into a hopper at the top of the furnace, and by lowering



Courtesy, Iron Trade Review.

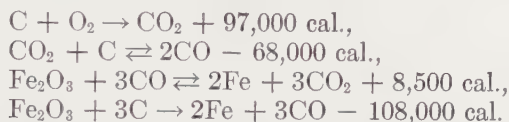
FIG. 191. Section of Blast Furnace, which Shows the Sequence of the Principal Reactions.

is partially reduced to carbon monoxide by the hot coke higher up in the furnace. The oxides of iron are reduced by carbon and carbon monoxide, the latter being very effective for the reason

a bell they are dropped into the furnace. The bell-shaped devices are so manipulated as to prevent the escape of furnace gases. Great volumes of dry pre-heated air are blown in through pipes called **tuyères**, near the bottom of the furnace. In ascending, the hot air acts chemically on the charge, the excess of gas (furnace gases) escaping through a large pipe (the "downcomer"). The furnace gases usually contain over 20 per cent of carbon monoxide by volume, and are utilized in pre-heating the blast and to drive the gas engines. Before utilization, the gases are freed of the large quantities of flue dust which they carry out of the furnace.

Some of the oxygen of the ascending air combines with coke in the lower part of the furnace, forming carbon dioxide, which

that it is a gas, and thus comes into very intimate contact with the ore. The principal chemical changes are shown by the following equations:



Some of these chemical changes are exothermic and others are endothermic.

As the reaction between the ore and carbon monoxide is reversible, a large excess of CO is necessary in order to complete the action. The temperature of the upper zone of reduction ranges from 300° to 900°, which is not hot enough to melt the iron. The spongy metal and any remaining oxides descend to the lower zone of reduction where the temperature is 900° to 1,200°. Here, further reduction takes place, the metal then descending to the zone of fusion (1,200° to 1,600°), through which the melting charge trickles down. The silica and alumina (clay) of the ore unite with lime to form a fusible slag. The molten iron collects in the bottom of the furnace (crucible), the lighter slag forming a layer above. The iron and the slag are tapped off periodically, the latter through a small opening called the cinder-notch. The iron is run into sand molds or iron molds, the product being known as **pig iron** or **cast iron**; or the molten metal is carried in large ladles to be converted into steel by the direct process, *i.e.*, without allowing the crude iron to solidify.

The **slag** is a complex silicate of calcium and aluminium. It may be granulated by pouring into water, and is utilized as ballast for railroads and in the manufacture of Portland cement. For the latter purpose, it is burned with more lime and then ground. In case the ore contains a basic gangue (limestone or dolomite), a siliceous or acidic flux is used instead of limestone.

A blast furnace is kept in continuous operation; it must be interrupted now and then in order to renew the linings.

The efficiency of the furnace is greatly increased by removing the moisture of the air before it goes to the stoves. (Why?) This is accomplished by means of a *refrigeration process*, the moisture being condensed and frozen on pipes containing cold brine. About 5 tons of air, previously heated to 800°, are required for each ton of iron produced.

The Trumbull-Cliffs Furnace of Warren, Ohio, produced 23,364 gross tons of iron during the month of January, 1923. This is an average of 754 tons per day. 1,986 pounds of coke per ton of iron were used.

The United States produces more than half of the world's pig iron. In the year 1918, over 38,000,000 tons were produced from our blast furnaces, the value being more than \$1,180,000,000. Our iron has a greater value than any other manufactured product, greater than that of all other metals combined. In sixty years the output of pig iron in the United States has increased from about 700,000 tons to approximately 40,000,000 tons annually. In 1926 the domestic production was 38,181,000 tons, valued at nearly \$750,000,000.

684. Properties and Uses of Pig Iron. — Pig iron, the product of the blast furnace, varies in composition and properties with the character of the ore and the operation of the furnace. In general, it may be stated that a pig iron contains from 3.5 to 4.5 per cent of carbon, from less than 1 to 3.5 of silicon, less than 1 per cent of manganese, varying amounts of phosphorus (practically all there is in the charge), and 0.02 to 0.1 per cent of sulfur. The percentage of iron is usually from 91 to 94. The presence of the impurities affects the properties of iron greatly. Thus, pure iron melts at $1,530^{\circ}$, whereas pig iron melts at from $1,150^{\circ}$ to $1,250^{\circ}$. Moreover, pig iron is hard and brittle and cannot be welded or forged. Carbon and silicon increase the hardness and strength; phosphorus, the fluidity, causing it to make better castings. Iron and steel, however, which contain phosphorus are "cold short," *i.e.*, brittle while cold, while those containing sulfur are

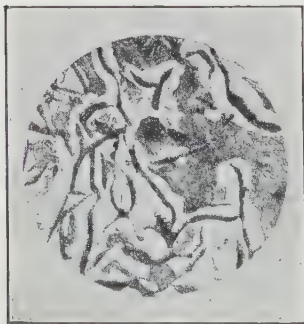
"red short," *i.e.*, brittle while hot. Furthermore, sulfur in iron tends to produce unsound castings. Manganese unites with sulfur to form manganese sulfide which passes into the slag.

There are *two commercial grades of pig iron*:

(1) **Gray iron.** This variety of pig iron is obtained by allowing the molten metal to cool slowly, thus affording time for the carbon to crystallize in large flakes of graphite. The iron is coarse-grained, and has a gray fracture (Fig. 192).

When dissolved in acids, graphitic carbon is left as a residue.

(2) **White iron.** White pig iron is produced by rapid cooling. The iron combines to a certain extent with carbon, forming an



Courtesy, Arthur D. Little, Inc.

FIG. 192. Gray Cast Iron.
× 250.

iron carbide (cementite), Fe_3C . This grade of iron is hard and brittle, and the color is much lighter than is that of gray iron. The cementite is in solid solution in the metal.

The following analyses of Cleveland pig iron show the difference in composition of these two varieties of iron:

	Gray	White
Carbon, Graphitic.....	3.20
Carbon, Combined.....	trace	3.05
Silicon.....	3.50	0.67
Phosphorus.....	1.76	1.60
Sulfur.....	0.05	0.40
Manganese.....	0.68	0.42

Note that the gray iron is high in silicon, as well as graphitic carbon. It melts to a thinner liquid and is better adapted for fine castings than is white iron.

Pig iron is melted in foundries and cast into various useful objects, such as stoves, radiators, etc. The larger part of pig iron is converted into steel, and a relatively small quantity into wrought iron.

685. **Wrought Iron.** — Wrought iron is manufactured by heating pig iron (or scrap iron) on the bed of a furnace of the reverberatory type. The furnace, called a **puddling furnace**, is lined with hematite or magnetite, which furnishes oxygen to burn out all but small amounts of carbon, silicon, manganese, phosphorus, and sulfur in the pig iron. The oxygen of the air also assists in removing the impurities. Heat is reflected and radiated from the dome of the furnace down upon the charge. The pig iron melts, but as the impurities are burned out, the melting point of the metal is raised until it finally forms a pasty mass. The metal is worked by a "puddler" by means of an iron rod, who finally gathers the iron into balls ("blooms") each weighing about 100 pounds. The pasty metal is worked under a steam hammer or in a mechanical squeezer in order to remove as much of the slag as possible. The bloom thus produced is rolled into muck bar. The product is soft and fibrous, and is called wrought iron. It often contains only 0.1 to 0.2 per cent of carbon, but there is more or less slag between the fibers of iron. Being very malleable and having great toughness and tensile strength, it is used in the manufacture of horseshoes, anchors, etc. In recent years wrought iron has been largely displaced by low-carbon (soft) steel.

The puddling process was invented by Henry Cort of England in 1784.

686. **Steel.** — Steel is manufactured from pig iron by two great processes, each of which may be subdivided into two divisions:

- | | | |
|---|---|--|
| (I) The Bessemer Process | { | (a) The Acid Bessemer Process |
| | | (b) The Basic Bessemer Process
(Thomas-Gilchrist) |
| (II) The Open-Hearth Process (Siemens-Martin) | { | (a) The Basic Open-Hearth Process |
| | | (b) The Acid Open-Hearth Process |

They are called the acid or the basic process, depending upon the character of the lining of the converter or furnace. In the acid process, silica or a siliceous material (acidic) is used as lining; in the basic process, a basic lining (*e.g.*, limestone, magnesite, or dolomite) is used.

Special steels are produced by the crucible and cementation processes. Steel is also produced by electric processes, electricity being converted into heat.

687. **The Bessemer Process.** — This process was invented by the Englishman Bessemer, in 1855. In 1852 an American named Kelly patented a similar process, but Bessemer bought Kelly's patents. The acid Bessemer process is extensively employed in the

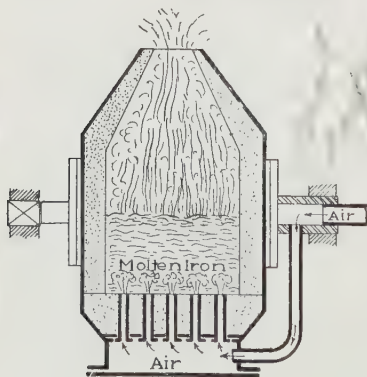


FIG. 193.

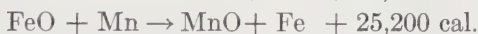
United States, and it is applicable to pig irons which are low in phosphorus and sulfur, for neither of these is removed during the operation. The vessels in which pig iron is converted into steel vary much both in size and shape, but the modern converters are so constructed that they may be rotated on their shorter axis through arcs of varying size; that is, they are of the tilting type, revolving on trunnions (Fig. 193.) The converter is constructed of steel, and lined

with silica or a siliceous refractory material. The capacity of converters ranges from 5 to 25 tons.

In operating a converter, usually 10 to 20 tons of molten pig iron are poured into the vessel while in the horizontal position, and an air-blast turned on, which enters the bottom of the converter through tuyères, and the vessel is then turned to the vertical position. *The air in passing up through the molten metal first oxidizes iron to the exclusion of the silicon, manganese, and carbon, FeO being formed:*



Silicon and manganese are then oxidized in turn by the ferrous oxide:



The excess of FeO and the MnO then interact with SiO₂ to form slag. The silicon and manganese are therefore oxidized indirectly, much heat being evolved and the metal kept in the liquid state.

When the silicon and manganese have been eliminated, the carbon is oxidized, and passes off largely as CO, which burns at the mouth of the converter, accompanied by a brilliant shower of sparks. In the course of 10 to 20 minutes nearly all the silicon, manganese, and carbon have been burned out.

When the character of the flame at the mouth of the converter indicates that practically all the carbon has been oxidized, the converter is turned down and the requisite amount of high-carbon alloy (e.g., *spiegeleisen*, 4 to 5 per cent of C and 10 to 20 of Mn; or *ferromanganese*, 6 to 7 C and 20 to 85 Mn) or coke is added to produce a steel of definite composition. The molten metal is now poured into molds and cast in ingots which are rolled or hammered into sheets, rails, bars, or other objects (Fig. 194). When the metal is poured into molds, more or less air is trapped in the liquid, so there is danger of weak places in steel rails or beams unless the gas bubbles are removed. "Deoxidizers" or "scavengers" are used for this purpose. Manganese has been employed extensively, but in recent years aluminium has been in great demand. Ferro-silicon and alloys of vanadium and of titanium are also used. "A.M.S." metal is an alloy of aluminium, manganese, and silicon; it is said to be a very efficient deoxidizer. These substances combine with the absorbed gases, and the resulting compounds pass into the slag.

The basic Bessemer process has been largely employed in Germany. The ores of that country contain more phosphorus than do the ores of the United

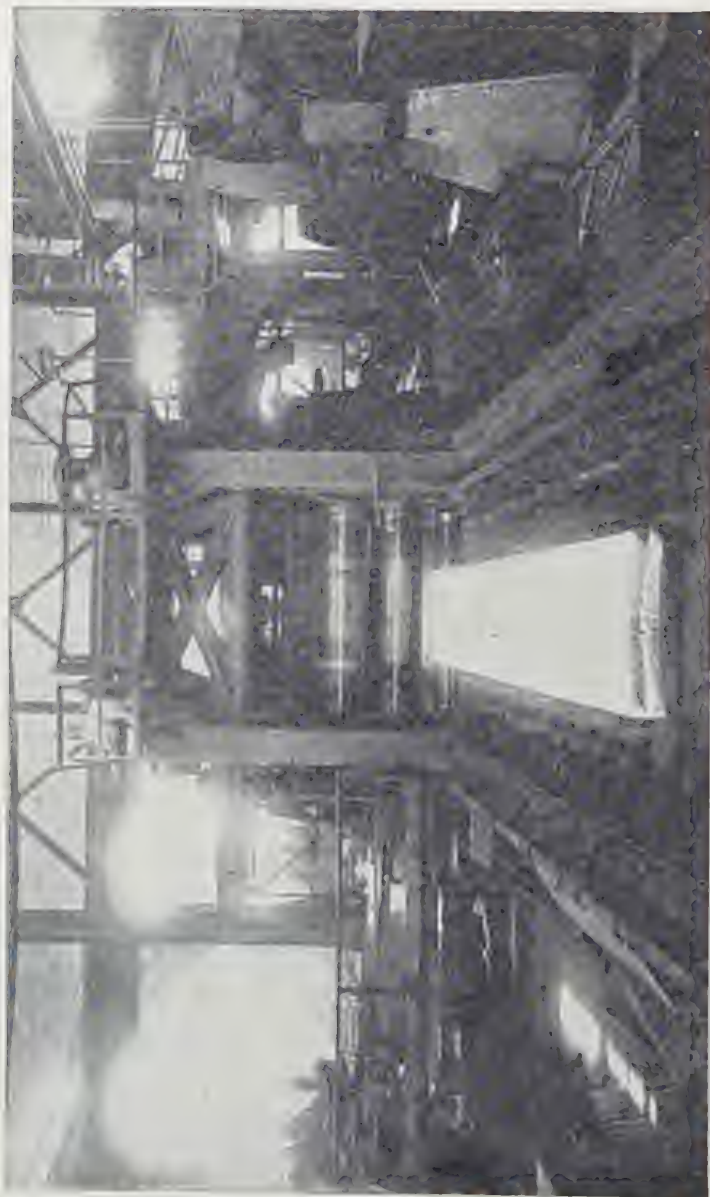


FIG. 194. Ingot Rolled into Slab — 32" Slabbing Mill.

Courtesy, Carnegie Steel Co.

States. The converter is lined with calcined dolomite or limestone, cemented with tar. A phosphate slag is obtained, which has some value as a fertilizer.

688. **The Open-Hearth Process.** — The basic open-hearth process is employed extensively in the United States. As the furnaces are lined with a basic material, usually magnesite, pig irons containing phosphorus may be used. The pig iron, scrap steel, and iron ore (*e.g.*, Fe_2O_3) are heated on the hearth of a regenerative, reverberatory furnace. The hearth of the furnace is about 40 feet long, 12 feet wide, and 2 feet deep. Heat is furnished by the combustion of gas or sprayed oil, and it is reflected and radiated upon the charge from the dome of the furnace (Fig. 195). The temperature of the operation is greatly increased by means of

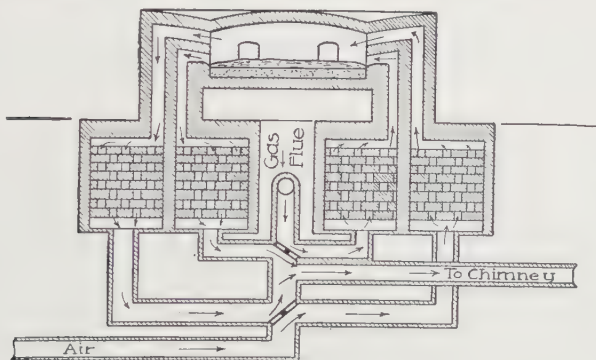


FIG. 195.

the **Siemens regenerative process**. This means that both the air and gaseous fuel (*e.g.*, producer gas) are preheated by passing through a checkerwork of hot brick. The checkerwork of brick is so placed that the hot products of combustion escaping from the furnace may be conducted through it. While the hot products of combustion are passing through one checkerwork of brick, the air and gas are passing through another. By frequently reversing the direction of the gases, it is possible to secure great economy in heating. Ordinarily, a furnace holds about 75 tons and about 8 hours are required for an operation. The carbon is oxidized to carbon dioxide, which escapes and gives the metal the appearance of boiling. Silicon, phosphorus, and sulfur are oxidized to anhydrides, which unite with the lining or flux to form a slag. When chemical tests show the desired amount of carbon to be present, the metal is poured into ladles, along with suitable quantities of

deoxidizers and alloys, and the liquid then run into molds. The oxygen of the rusty scrap iron or ore is used in burning out the impurities. The steel is of high grade.

The gross tonnage of steel ingots and castings manufactured in the United States for the years 1914 and 1918 was as follows:

	1914	1918
Open-Hearth process.....	17,170,000	34,460,000
Bessemer process.....	6,220,000	9,380,000
Total production.....	23,390,000	43,840,000

In 1925 the domestic production of steel ingots was over 44,000,000 tons, and in 1926 it was greater still.

The open-hearth process is rapidly replacing the Bessemer process, about 80 per cent of the steel being produced by the former.

On January 1, 1919, the domestic capacity for manufacturing steel ingots was close to 50,000,000 tons, which was estimated to be about 48 per cent of the world's facilities for producing steel.

689. Crucible Steel.—Special steels are required for the manufacture of razors, tools, cutlery, files, needles, etc. The production of these steels is carried out in crucibles of clay, or of clay and graphite. A very pure open-hearth steel or wrought iron is melted with charcoal and pure pig iron, or with an alloy of iron and manganese. Other metals, such as chromium, nickel, tungsten, etc., may be added if desired. The crucibles are covered and heated for several

hours. This method gives a homogeneous steel, which is free from occluded slag and dirt.

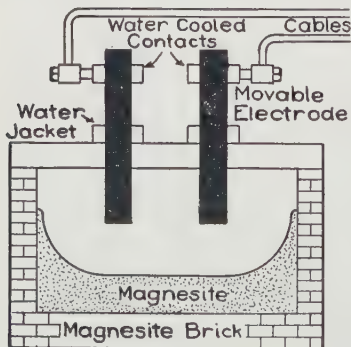


FIG. 196.

690. Electric Steel.—Considerable steel of superior quality is now produced by electric heating. Electric-furnace refining produces high-class steel for special purposes. As the operation is carried out at very high temperatures, the impurities are more completely removed, especially gases.

Phosphorus and sulfur are almost completely eliminated, and de-oxidation is more complete than that attained by other processes. This method is rapidly replacing the crucible process for pro-

ducing tool steel. It is somewhat similar to the open-hearth process, but heat is generated by electricity instead of by the combustion of fuel.

The **Heroult furnace** is the leading one employed for the manufacture of steel, because of its efficiency, simplicity, and adaptability (Fig. 196).

In 1908 only 55 tons of electric steel were produced in the United States, but in 1923 the production had risen to nearly 516,000 tons. It may be that in the course of time the electric furnace will replace the open-hearth process, very much as the latter is replacing the Bessemer process. Since some of the modern electric furnaces hold 20 tons and can readily make ten heats in twenty-four hours, the total production would be equal to that of a 100-ton open-hearth furnace making but two heats in twenty-four hours.

691. Composition of Steel. — The following figures will serve to show the composition of an ordinary pig iron as well as of Bessemer and open-hearth steel:

	Pig Iron	Bessemer Steel	Basic Open-Hearth Steel
Iron, Fe.....	93.0	98.366	99.155
Carbon, C.....	3.5	0.460	0.366
Silicon, Si.....	2.0	0.087	0.012
Manganese, Mn...	1.0	0.910	0.419
Phosphorus, P....	0.10	0.102	0.012
Sulfur, S.....	0.08	0.069	0.036

These analyses were made by the Bureau of Standards at Washington. The percentage of iron was obtained by difference.

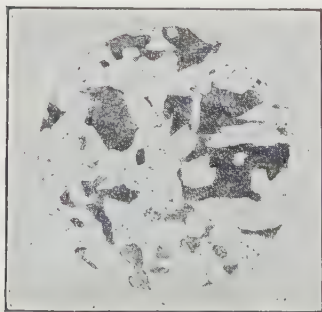
Steel may contain from about 0.03 per cent up to about 2 per cent of carbon, less than 0.2 per cent of silicon, and very small amounts of phosphorus and sulfur. Steel low in carbon is soft. Thus, steel containing 99.85 per cent of iron is manufactured by the open-hearth process; it is very soft. By an increase in the carbon content of a steel, it is made harder and less ductile, and the tenacity increases until the carbon reaches about 1.1 per cent, after which it decreases. Some rail steel contains as much as 0.8 per cent of carbon. Tool steel contains from 0.5 per cent to 1.5 per cent of carbon, but contains almost no phosphorus and silicon. It is not necessary that steel contain less than 0.2 per cent of silicon. Manganese is an essential constituent of steel.

692. The Hardening and Tempering of Steel. — A high-carbon steel (0.5 to 1.5 per cent of C) becomes very hard and brittle when

heated to a high temperature and then suddenly chilled, as when plunged into cold water or oil. This hardness and brittleness may be modified to almost any degree desired by tempering the hardened product. This consists in gradually heating the steel to a moderately high temperature and then allowing it slowly to cool. By this treatment the steel becomes less hard and less brittle. By regulating the heat treatment and the carbon content, a steel of practically any desired degree of hardness may be obtained. For example, steel for razors, surgical instruments, etc., requires the hardest temper, which is obtained at a temperature of about 230° (Roscoe).

Case-hardening of steel may be accomplished by heating a soft steel or wrought iron in contact with powdered carbon. The latter is slowly taken up, producing a layer of hard high-carbon steel on a body of softer metal. This process (or a similar one) is employed for hardening the surfaces of automobile gears, etc., and for the manufacture of armor-plate.

The heat-treatment of steel is made easier and better physical properties are developed when certain alloying elements, notably nickel, chromium, vanadium, or molybdenum, or a combination of two or more of these, are present.



Courtesy, Arthur D. Little, Inc.

FIG. 197. Low Carbon Steel.
 $\times 250$

Heat-treated alloy steels are essential for all present-day automobiles, aircraft, and high-speed machinery in general.

The microscope and photography have become very important in the study of the structure of metals and alloys. When the surface of iron or of steel is polished and then carefully etched by means of acids, something may be learned about the characteristic crystalline formations. **Photomicrographs** (Fig. 197) are made, and the relation of crystalline forms to physical properties may be studied. This branch of science is called **metallography**.

In order to understand the tempering of steel it is necessary to know that iron exists in several allotropic forms, such as

α -iron, β -iron, and γ -iron. When iron is cooled, certain temperature fluctuations are observed which are presumably due to the transition of iron from one allotropic form to another. The physi-

cal and mechanical properties of the iron correspond with the transition temperatures. When cold iron is heated, the sequence of changes is reversed. It appears, therefore, that there are energy changes in passing from one allotropic modification to another.

α -iron is pure iron (*ferrite*), and therefore makes up nearly the whole of wrought iron. It is stable below about 750° , has a cube-centered cubic lattice (64), is soft, ductile and magnetic, deficient in tensile strength, and possesses virtually no hardening power.

When α -iron is heated through 900° , γ -iron is formed, a complete recrystallization taking place. This form of iron, like copper and gold, has a face-centered cubic lattice (64); it is hard, ductile, and non-magnetic.

Iron melts at $1,530^{\circ}$ and dissolves carbon, some of the latter being present in solution as free carbon and some as iron carbide, or cementite.

When white-hot steel containing up to 2 per cent of carbon is suddenly chilled, a supersaturated solid solution is formed, for the carbon and cementite do not have time to separate out. This gives a hard, brittle product. In case the metal is allowed slowly to cool, some of the carbon separates out as graphite along with cementite, giving a saturated solid solution. Carbon is not soluble in α -iron, the form of iron stable at ordinary temperatures, but is soluble in γ -iron.

When liquid iron containing less than 4.2 per cent of dissolved carbon is cooled, the solid which first separates is a solid solution known as *austenite*; it contains carbon or iron carbide dissolved in γ -iron. When austenite containing more than 0.9 per cent of carbon is cooled, it yields cementite; but if it contains less carbon, α -iron or β -iron¹ is formed. The eutectic temperature (177 and 597) is 690° , and the eutectic mixture of α -iron and cementite is called *pearlite*.

The properties of a steel are dependent upon its chemical composition and upon whether it has been rapidly or slowly cooled. Certain alloying elements (*e.g.*, manganese) greatly reduce the facility with which γ -iron changes into α -iron.

Summing up, we may state that there are distinct crystalline forms of iron, each being stable through a certain range of temperature. Moreover, there are definite temperatures or transition points at which these allotropic forms are in equilibrium, just as

¹ β -iron is not very important. It exists only within a narrow range of temperature (approximately from 750° to 900°).

gray tin is in equilibrium with white tin at the transition point 13° (597). Carbon may be present in iron —

- (1) In solution in the liquid;
- (2) In solution in crystals of γ -iron;
- (3) In the form of a carbide, Fe_3C ;
- (4) As free graphitic carbon.

The properties of iron are greatly influenced by small quantities of carbon.

The hardening and tempering of steel is of the highest importance. While vast improvements have been made in the methods of producing steel, no improvement has been made recently in its quality; the old blades of Toledo and of Damascus have never been excelled.

693. Steel Alloys. — A large number of steel alloys are manufactured for various purposes. *An alloy steel contains, in addition to carbon, one or more other elements in sufficient amounts to modify the properties of the steel to a marked degree over a carbon steel.*

Manganese increases the toughness of steel. Steels containing over 1 per cent and less than 7 per cent of manganese are used in the construction of machines and for certain tools. Steels containing over 7 per cent of the element are used in the jaws of rock-crushers, in burglar-proof safes, in railroad crossings, etc.

Nickel increases the tenacity and hardness of steel. Steels containing more than 0.5 per cent of nickel are employed as structural steels. Armor-plate contains from 3 to 5 per cent of the metal.

Chromium increases the hardness and lessens the tendency to corrode. It is valuable in tool steels and in armor-plate. "Stainless" steel contains the following:

Chromium.....	12–15 per cent
Carbon.....	0.25–0.4 per cent
Manganese.....	0.20–0.45 per cent
Silicon.....	0.20–0.3 per cent
Sulfur and Phosphorus.....	not more than 0.03 per cent

Chromium-vanadium steel has great tensile strength.

Tungsten steel is used for magnets and for high-speed tools.

Vanadium steel (0.15 to 0.25 per cent of vanadium) is excellent for tools and machinery.

Molybdenum and cobalt, as well as tungsten, prevent the loss of the temper of the steel when heated to a high temperature.

Silicon forms alloys (*e.g.*, *duriron* or *tantiron*) which resist acids.

694. Properties of Iron. — Pure iron possesses a luster which is practically silver-white; it has a density of 7.86 and melts at $1,530^{\circ}$. Iron is attracted by the magnet; it may also be rendered magnetic, but it loses its magnetism readily. Iron, unlike steel, cannot be hardened by sudden cooling. Pure iron is of no practical value. The pure metal may be obtained by reducing pure oxides of iron by hydrogen, or by the electrolysis of a boiling solution of ferrous sulfate (FeSO_4) between iron electrodes, which yields a product containing 99.98 per cent of iron.

Chemically, iron is a fairly active metal, standing just below zinc. Thus, it displaces hydrogen readily from dilute acids. Pure iron rusts very slowly in pure water at ordinary temperatures. With water containing carbon dioxide in solution, the corrosion is greatly increased (see Couples, 617). The metal may be protected from rusting by coating it with ochre, Fe_2O_3 , or with Fe_3O_4 (*Russian iron*). Iron rust is hydrated ferric oxide, $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$. Metallic coatings, such as zinc, tin, chromium, nickel, and copper, also afford protection. Enamels, asphalt, red lead, vaseline, and lubricating oil are also employed.

Heated iron burns in oxygen, forming the magnetic oxide, Fe_3O_4 . Iron is indifferent to fuming nitric acid. When the metal has been treated thus, it is called *passive iron*. Iron in the passive state is indifferent to both dilute and concentrated nitric acid, which attack ordinary iron. Passive iron loses its passivity when scratched or when given a sharp blow.

Iron forms two series of compounds; namely, (a) *ferrous compounds* (*e.g.*, FeO , $\text{Fe}(\text{OH})_2$, FeCl_2 , etc.) and (b) *ferric compounds* (*e.g.*, Fe_2O_3 , $\text{Fe}(\text{OH})_3$, and FeCl_3).

695. Ferrous Compounds. — **Ferrous oxide**, FeO , may be obtained by heating ferrous oxalate, FeC_2O_4 , with the exclusion of air or oxygen.

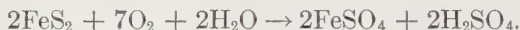
Ferrous hydroxide, $\text{Fe}(\text{OH})_2$, may be obtained as a white flocculent precipitate by treating a solution of a ferrous salt with an alkali, oxygen being excluded; it readily absorbs oxygen, turning dark green, and finally forming reddish-brown ferric hydroxide, $\text{Fe}(\text{OH})_3$.

Ferrous sulfide, FeS , is prepared by heating iron and sulfur together. The compound is also obtained as a black precipitate by treating a solution of a ferrous salt with an alkaline sulfide. It dissolves in acids, forming hydrogen sulfide.

Ferrous chloride, FeCl_2 , may be obtained as white, feathery crystals by heating iron in a current of hydrogen chloride.

Ferrous carbonate, FeCO_3 , occurs in nature as the mineral siderite; it is an important ore of iron.

Ferrous sulfate, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, is often called **green vitriol**, or **copperas**. This salt may be obtained by dissolving iron in dilute sulfuric acid, with the exclusion of air or oxygen, and by concentrating the solution until crystallization occurs. It is also manufactured by the oxidation of iron pyrites:



The salt is used in the purification of water, in the dyeing industry, as a reagent for killing weeds, and in the manufacture of black inks.

Inks are commonly produced by adding ferrous sulfate to an extract of nut-galls, ferrous tannate (colorless) being formed, which is oxidized, when exposed to the air, to ferric tannate (black). A dye is added to the ink to make it visible from the first.

Inks were prepared from iron salt and nut-galls many centuries ago, and were undoubtedly used by early authors in writing on parchment. In case the writing has become illegible, due to the fading of the ink, it may be restored by treating the manuscript with a dilute solution of ammonium sulfide. The writer treated a very valuable manuscript of the 14th century thus, and obtained remarkable effects.

Ink stains and *rust stains* may be removed by soaking the material in ammonium oxalate solution.

Ammonium ferrous sulfate, or **Mohr's salt**, $(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}$, is used in analysis as a reducing agent.

696. Ferric Compounds. — **Ferric oxide**, Fe_2O_3 , occurs abundantly as the mineral hematite; it may be prepared by heating the hydroxide, $\text{Fe}(\text{OH})_3$. The pigment called *Venetian red* is ferric oxide; it is extensively used for painting bridges, roofs, railway cars, etc. The hydrated oxide constitutes brown hematite and iron rust.

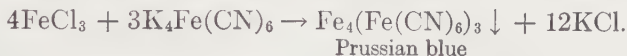
Magnetite, Fe_3O_4 , appears to have the structure of a spinel (589). The compound is sometimes called *ferroso-ferric oxide*. It furnishes a good coating for iron to protect against rusting.

Ferric chloride, FeCl_3 , is obtained by the interaction of iron and chlorine. The anhydrous salt may be volatilized without decomposition. It is very soluble in water and the solution has an acid reaction (explain). An alcoholic solution of the salt is sold as tincture of iron.

Ferric iron enters into the composition of the ferric alums.

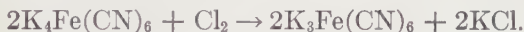
697. **Ferro- and Ferricyanide of Potassium.** — **Potassium ferrocyanide** ("yellow prussiate of potash"), $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$, can be obtained by igniting a mixture of nitrogenous organic matter, potassium carbonate, and scrap iron, and then treating the mass with hot water, from which the salt separates as yellow crystals. It is a salt of **hydroferrocyanic acid**, $\text{H}_4\text{Fe}(\text{CN})_6$.

When a solution of potassium ferrocyanide is treated with a ferric salt, **ferric ferrocyanide**, or **Prussian blue**, is obtained:



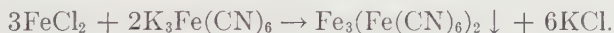
Prussian blue is used as a pigment and for the preparation of "blueing" for the laundry.

Potassium ferricyanide, $\text{K}_3\text{Fe}(\text{CN})_6$, is often called "red prussiate of potash." It is formed when potassium ferrocyanide is treated with oxidizing agents:



It is obtained as large dark-red, anhydrous crystals. Its aqueous solution contains the trivalent ion $\text{Fe}(\text{CN})_6^{=}$.

Ferrous salts yield with potassium ferricyanide a dark blue precipitate of **ferrous ferricyanide**, or **Turnbull's blue**:



698. **Blue-Prints.** — Ferric salts of certain organic acids can be reduced to ferrous salts by exposure to light. The production of blue-prints is based upon this reaction. Thus, ferric oxalate, $\text{Fe}_2(\text{C}_2\text{O}_4)_3$, yields ferrous oxalate, FeC_2O_4 :



Paper can be prepared by treating it with a solution of ferric oxalate and then drying. When an ink drawing or a negative is placed over a paper thus prepared, sunlight will reduce only the exposed ferric oxalate to ferrous oxalate. When the paper is now dipped in a solution of potassium ferricyanide (developer), blue ferrous ferricyanide (Turnbull's blue) is formed where the sheet has been exposed to the light. Where the paper has not been exposed to the light, no change occurs, and the ferric salt can be washed away. There is thus left a white pattern or picture on a blue background; that is, a blue-print is obtained.

Commercially, blue-print paper is coated with a mixture of ammonium ferric citrate and potassium ferricyanide (developer). After exposure to light, the paper is dipped into water, and the blue color quickly appears. The sheet is now washed, giving a permanent print.

COBALT. Co = 58.94

699. **History and Occurrence.** — Cobalt (German, *kobald*, goblin) was discovered by the Swedish chemist Brandt, in 1735, who stated that the blue color of smalt depends upon the presence of this metal. He also stated that cobalt is magnetic and extremely infusible. Bergman, in 1780, confirmed these observations.

Cobalt usually occurs in combination with arsenic and sulfur in complex minerals also containing iron, nickel, and copper. The richest deposits of cobalt minerals are at Cobalt, Ontario. Some cobalt was produced in the United States in 1918, but the metal and its oxide are largely imported from Canada. In the district surrounding the town of Cobalt there are rich silver ores containing considerable cobalt and nickel, chiefly as arsenides. The cobalt minerals include —

Smaltite (cobalt arsenide).....	CoAs ₂ ,
and Cobaltite (arsenide-sulfide).....	CoAsS

700. **Metallurgy and Uses.** — Metallic cobalt is obtained by igniting the oxide in a current of hydrogen or carbon monoxide, by reduction with carbon or aluminium, or by smelting the ore in a blast furnace. The charge of the furnace consists of the ore mixed with an appropriate flux and fuel.

701. **Properties and Uses.** — The properties of cobalt are somewhat similar to those of iron, but it is more closely related to nickel.

Cobalt is used in the manufacture of high-speed steel, of which it may constitute over 50 per cent. **Stellite**, an alloy of cobalt, chromium, and tungsten, is used in manufacturing lathe tools and surgeon's and dentist's knives. This alloy has remarkable non-oxidizing properties, and offers great resistance to change under heat. During the war, army surgeons in France sterilized their instruments constructed of stellite by holding them in a flame. Neither the edge nor the polish of the instrument was destroyed.

Cobalt is also used for electroplating. The plate is more ad-

herent and durable than that of nickel. Cobalt steel for high-speed tools has been produced at Sheffield. It has the advantage of not undergoing distortion in hardening. Cobalt steel for permanent magnets (*e.g.*, magnetos for ignition purposes in aircraft) is promising.

Cobalt oxide, CoO , is used for coloring glass, decorating china, and in preparing other cobalt compounds. Smalt (a blue pigment) is a sort of cobalt glass.

702. Compounds. — Both cobaltous and cobaltic compounds are known.

Cobaltous chloride, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, and cobaltous nitrate, $\text{Co}(\text{NO}_3)_2$, are cherry-red soluble salts, frequently used in the laboratory.

Cobaltous sulfide, CoS , is a black compound obtained by treating a cobaltous salt with ammonium sulfide. It is readily soluble in aqua regia.

The cobaltous ion (Co^{++}) is pink. Hydrated cobaltous salts are generally pink, while the anhydrous salts are blue (sympathetic ink).

Cobaltous salts yield the sparingly soluble yellow **potassium cobaltinitrite**, $\text{K}_3\text{Co}(\text{NO}_2)_6$, when treated with potassium nitrite in the presence of acetic acid. It is used as a pigment (cobalt yellow).

Cobaltic salts yield, with ammonia, many and various complex compounds known as the **cobalt ammines**: *e.g.*, $\text{Co}(\text{NH}_3)_6\text{Cl}_3$, hexammine-cobaltic chloride (see Copper, 522).

Hopcalite is a mixture of the oxides of cobalt, manganese, copper, and sometimes silver; it is employed as a catalyst in gas masks in order to oxidize carbon monoxide, which is not removed by ordinary adsorbents.

NICKEL. $\text{Ni} = 58.69$

703. History and Occurrences. — Nickel was discovered by the mineralogist Cronstedt in 1751.

Nickel almost always occurs associated with cobalt. The most important nickel-bearing ores are found in the Sudbury district, Ontario. Considerable nickel also occurs in New Caledonia. In Ontario nickel occurs largely as the sulfide, known as

Pentlandite $(\text{Ni}, \text{Fe}, \text{Cu})\text{S}$.

In New Caledonia it occurs as a hydrated silicate of nickel and magnesium.

704. Metallurgy and Uses. — The metallurgy of the element is complicated, the method adopted depending upon the nature of the ore. For the sulfide ores of Canada, the treatment is as follows:

- (1) The ore is first heap-roasted to oxidize iron and sulfur.
- (2) The roasted ore is then smelted in a blast furnace to produce a matte (36 to 40 per cent Ni + Cu).
- (3) This matte is then bessermized to a matte containing about 80 per cent of Ni + Cu and nearly 20 per cent of S. There are different processes for producing nickel from the Ni-Cu matte. In the **Mond process**, the metal is converted into nickel carbonyl Ni(CO)_4 , which decomposes at about 200°C ., yielding nickel. Nickel and copper may also be separated by electrolysis.

Monel metal is an alloy of nickel and copper produced directly from the Ni-Cu matte of the Sudbury ores. It contains from 60 to 72 per cent of Ni, as well as Cu, Fe, and Mn. It is largely used for sheet-metal work, being stronger than ordinary steel and having valuable acid-resisting properties.

Nickel is a whitish metal with a tinge of yellow. It has a density of 8.7, melts at $1,452^\circ$, and is malleable, ductile, and magnetic. The metal rusts slowly in moist air, and is very resistant to the attack of hot alkalis; it is difficult to oxidize, displaces hydrogen with difficulty, but dissolves in nitric acid to form the nitrate.

Nickel is used extensively in alloys: *e.g.*, in the manufacture of steel, coinage (Ni, Cu), German silver, invar (a steel with about 36 per cent of Ni), Monel metal (alloy of Ni and Cu). **Invar** has an exceedingly low coefficient of expansion when heated, and is very valuable for pendulum rods and meter-scales. The metal is also used extensively in electroplating, a bath of pure **ammonium nickel sulfate**, $(\text{NH}_4)_2\text{SO}_4 \cdot \text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, being employed.

It is important to know that **nickel-chromium alloys** offer great resistance to corrosion, and are able to withstand high temperatures without oxidation. These alloys also have high electrical resistance, and their development has made possible electrical toasters and other domestic appliances, as well as many commercial applications of electric heat. **Nichrome** (Ni, Cr, Fe, Mn) is a very useful alloy. Nickel is an important catalyst.

Permalloy contains nickel and iron. A typical alloy of this type contains about 80 per cent of nickel to 20 per cent of iron. When permalloy is properly heat-treated, it possesses remarkable magnetic properties, being easily magnetized by the magnetic fields produced by feeble currents.

705. Compounds. — Nickel forms only one series of salts, — the nickelous: *e.g.*, NiCl_2 , NiSO_4 , $\text{Ni}(\text{NO}_3)_2$, etc.

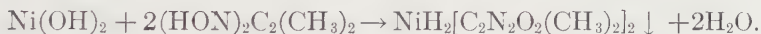
Nickel sulfate, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, and nickel-ammonium sulfate (see above) are the most common salts of the metal.

Nickel-ion, Ni^{++} , is green, and in many respects is similar to the cobalt-ion, Co^{++} . Thus, both interact with the sulfide-ion, yielding black sulfides (NiS and CoS).

The crystallized salts of nickel, as well as their aqueous solutions, are green, while the anhydrous salts are usually yellow. The sulfide, carbonate, and phosphate are insoluble in water.

Nickel carbonyl, $\text{Ni}(\text{CO})_4$, is a colorless liquid, which boils at about 43° . The compound is decomposed by heat, being explosive at 60° . The vapor is highly poisonous. One method for the preparation of nickel is based upon heating this compound.

When an ammoniacal solution of nickel is treated with **dimethylglyoxime**, $(\text{HON})_2\text{C}_2(\text{CH}_3)_2$, a brilliant scarlet precipitate is obtained:



When cobalt is thus treated no precipitate is obtained. Nickel is not precipitated by potassium nitrite in acetic acid solution. These reactions are used by chemists for separating nickel and cobalt.

706. Analytical. — When a neutral or an alkaline solution containing salts or ions of iron, cobalt, and nickel is treated with hydrogen sulfide, the metals are precipitated as the sulfides, which are black. Ferrous sulfide may be separated from the other sulfides by treating the mixed sulfides with dilute hydrochloric acid. The sulfides of cobalt and of nickel are soluble in aqua regia, but only sparingly soluble in dilute hydrochloric acid.

Ferrous compounds yield a blue precipitate (Turnbull's blue) with potassium ferricyanide, $\text{K}_3\text{Fe}(\text{CN})_6$, and no coloration with potassium thiocyanate, KCNS .

Solutions of ferric compounds, which may be obtained by oxidizing ferrous compounds, interact with a solution of potassium ferrocyanide, $\text{K}_4\text{Fe}(\text{CN})_6$, to form a blue precipitate (Prussian blue); they yield a blood-red coloration when treated with potassium or ammonium thiocyanate (KCNS or NH_4CNS).

When a cobalt compound is heated in the borax bead, a fine blue color is obtained. Nickel compounds give a brown bead in the oxidizing flame, while in the reducing flame the bead becomes gray.

As seen above, nickel yields a fine scarlet precipitate with dimethylglyoxime, while cobalt does not.

EXERCISES

1. Name the elements of the Iron Family, show their relationships, and state their general characteristics. Why are they sometimes called "transitional elements"?

2. Arrange the following elements according to their increasing atomic numbers, and compare and contrast some of their properties: iron, nickel, cobalt, manganese, and chromium.

3. Can you state any theory which satisfactorily explains the variable valence of such elements as iron, chromium, and manganese?

4. Outline the metallurgy of iron. What is the approximate composition of pig iron, and what are its properties?

5. Explain how pig iron may be converted into wrought iron, stating the principle involved.

6. Describe the acid Bessemer process and the basic open-hearth process for the manufacture of steel. What advantages has the latter process over the former?

7. Discuss the chemical changes involved in converting iron ores into pig-iron and the latter into steel. Compare the composition of pig-iron with that of steel.

8. What are the properties of steel? What is the difference between soft and wrought iron? How is steel hardened and tempered? How does the carbon content affect the properties of steel?

9. Give the names, approximate composition, and the uses of a number of steel alloys. What are "deoxidizers" or "scavengers"? Mention some which are particularly effective.

10. Aqueous solutions of ferrous salts are less hydrolyzed than are those of ferric salts. Explain.

11. How would you differentiate between ferrous and ferric compounds?

12. Outline the chemistry of blue-prints.

13. How may potassium ferrocyanide be changed into potassium ferricyanide?

14. Starting with iron pyrites, show how ferric ammonium alum could be prepared.

15. Give the occurrence, properties, and uses of cobalt. What is stellite?

16. Outline the occurrence, properties, and uses of nickel.

17. How may cobalt and nickel be separated and identified?

18. What are sympathetic inks?

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CHAPTER XXXIX

THE PLATINUM METALS

707. **Relationships and General Characteristics.** — Group VIII of the Periodic System contains, as already stated (81), three sub-groups or triads of metals. The following table contains the elements in the second and third groups, together with their atomic weights, atomic numbers, densities, melting points, and boiling points:

Element	Atomic Weight	Atomic Number	Density	Melting Point	Boiling Point
{ Ruthenium, Ru	101.7	44	12.30	2450°	2700°
{ Rhodium, Rh...	102.91	45	12.44	1955°	2500°
{ Palladium, Pd...	106.7	46	11.40	1555°	2200°
{ Osmium, Os....	190.8	76	22.50	2700°	5300°
{ Iridium, Ir.....	193.1	77	22.41	2350°	4800°
{ Platinum, Pt...	195.23	78	21.40	1755°	4300°

The six “precious metals” of the platinum family have many similar properties; therefore it is difficult to separate them from one another. They also resemble gold (Chap. XXIX).

Platinum and its allied metals are greyish white, heavy, difficultly fusible, possess little reactivity and therefore offer great resistance to corrosion. Owing to their lack of activity, they are easily separated from their compounds and are found in nature in the free state.

Ruthenium, *rhodium*, and *palladium* constitute the second triad of Group VIII; and *osmium*, *iridium*, and *platinum* form the third triad. Certain natural relationships are exhibited by the pairs — ruthenium and osmium, rhodium and iridium, palladium and platinum. Thus, palladium and platinum occlude hydrogen (123); and ruthenium and osmium form oxides of the type MO_4 , in which the metal has a valence of eight.

The oxides of the platinum metals possess neither decidedly basic nor acidic characters. They have a *multiple valence*, which is illustrated by the following compounds:

RuO	Ru ₂ O ₃	RuO ₂	RuO ₄	RuCl ₂	RuCl ₃	RuCl ₄
RhO	Rh ₂ O ₃	RhO ₂			RhCl ₃	
PdO		PdO ₂		PdCl ₂		PdCl ₄
OsO	Os ₂ O ₃	OsO ₂	OsO ₄	OsCl ₂	OsCl ₃	OsCl ₄
	Ir ₂ O ₃	IrO ₂		IrCl ₂	IrCl ₃	IrCl ₄
PtO		PtO ₂		PtCl ₂		PtCl ₄

The metals of the platinum family show a marked tendency toward the formation of complex ions, such as PtCl_6^- . Platinum is the most important element of the family.

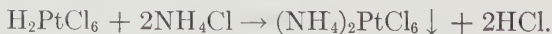
708. Occurrence. — As a rule, platinum and its allied metals are found native and associated together. They usually occur in magnesium rocks, or in gravels derived therefrom. Chromite and the ores of nickel often accompany platinum. **Sperryite**, PtAs_2 , is found at Sudbury, Canada (703).

The platinum metals occur principally in the Ural Mountains of Russia, in Colombia, and in the Transvaal. They also occur in New South Wales and Tasmania, in the Pacific Coast States, in Borneo, in Canada, and in Brazil. These elements are rather rare. The native alloy usually contains from about 60 to 84 per cent of platinum.

PLATINUM. Pt = 195.23

709. History and Preparation. — **Platinum** (Spanish, *platina*, dim. of *plata*, the Spanish for silver) appears to have been observed in the sixteenth century; but it did not attract general attention until the eighteenth century. About 1750 it was examined by Watson, by Brownrigg, and by Scheffer, being termed by the last "white gold," or "*platina del Pinto*," i.e., small silver of Pinto.

Platinum is usually prepared by first dissolving the ore or native alloy in aqua regia, and then evaporating the solution to dryness, chloroplatinic acid (H_2PtCl_6) being obtained. The residue is dissolved in water, acidified with hydrochloric acid, filtered, and the platinum precipitated as **ammonium chloroplatinate** by the addition of ammonium chloride:



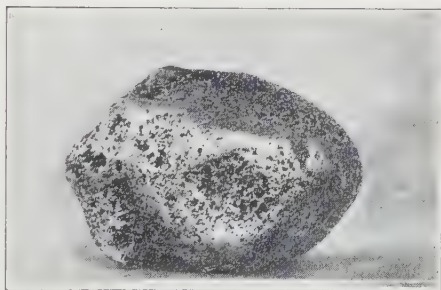
Part of the iridium is also precipitated in the form of a similar compound. By igniting $(\text{NH}_4)_2\text{PtCl}_6$, spongy platinum is obtained, which may be fused in the electric furnace or by the oxy-hydrogen flame, a lime crucible being employed.

As a rule, the platinum of commerce is not pure; it usually contains about 2 per cent of iridium. This alloy was formerly used

in Russian coinage, and is very valuable for chemical ware, as it is more resistant to acids than is pure platinum.

The Ural mines were first opened in 1825, only 361 pounds of platinum being produced. Before that date platinum came chiefly from South America. From 1911 to 1914, the estimated world's production of crude platinum averaged annually approximately 290,000 troy ounces, of which Russia produced over 94 per cent and Colombia nearly 5 per cent. The United States averaged about 600 troy ounces, which was only slightly increased during the years of the war. In 1924 the domestic production was about 4,200 ounces.

710. Properties of Platinum. — Pure platinum (Fig. 198) has a tin-white color, a density of 21.4, and melts at $1,755^{\circ}$. It is one of the most malleable and ductile of the metals (480), and can be welded at a white-heat. The metal forms solid solutions with such metals as gold, iron, and copper, which are usually harder than the constituent metals. Thus, gold is hardened by adding about 10 per cent of platinum; this alloy is used for making gold springs in dentistry. Platinum is a good conductor of electricity.



Courtesy, Baker & Co., Newark, N. J.

Finely divided platinum, or spongy platinum, wire of small diameter, adsorbs or condenses certain gases (123). Thus, a mixture of hydrogen and oxygen will explode in the presence of platinum (catalyst). Platinum also condenses the vapor of methyl alcohol. Certain gas-lighters and cigar-lighters are constructed on this principle (explain more fully).

FIG. 198. Platinum Nugget, South America, 1896. $47\frac{1}{2}$ per cent of original size. Full size, weight = 20.402 ounces.

Hydrogen gas passes through hot sheet platinum. It is not safe, therefore, to heat in a gas flame any readily reducible oxide in a platinum crucible. Platinum has almost the same coefficient of expansion as glass.

Platinum retains its luster when heated to high temperatures in air or oxygen or in contact with water. It is scarcely attacked by hot nitric acid, but is appreciably attacked by hot concentrated sulfuric acid. The metal dissolves readily in aqua regia and inter-

acts with chlorine to form the tetrachloride (PtCl_4). It is attacked by fusion with the caustic alkalis or nitrates, by alkali cyanides, phosphorus, arsenic, antimony, etc. Great care should be exercised, therefore, in the use of platinum ware.

711. Uses. — According to Hill, “the essential uses of platinum metals are in the chemical and electrical industries, and probably their use by the dental industry should also be classed as essential.”

Platinum is used extensively as a catalyst in the manufacture of sulfuric acid by the contact process (338), and platinum gauze is employed as catalyst in the manufacture of nitric acid (387). Platinum dishes, crucibles, tongs, foil, wire, etc., are required in the chemical laboratory. No substitutes will entirely replace platinum in chemical ware, but certain *substitutes* are satisfactory for special purposes, among which are the following:

Palau, an alloy of palladium and gold.

Rhotanium, an alloy of gold, palladium, and rhodium.

Tungsten is used especially for spark contacts.

Quartz dishes are used in the chemical industries.

Alloys of Nickel and Chromium are used for electrical-resistance heaters.

Platinum is so scarce and is such a necessary metal in time of peace as well as in war, that its use in jewelry should be reduced to a minimum or perhaps discontinued. Before the war the average consumption of the platinum metals in the United States was about 165,000 ounces, of which it was estimated that the jewelry and dental industries used 75 per cent, the electrical industry 20 per cent, and the chemical industry 5 per cent. This makes it clear why the stocks of the larger producers of platinum were requisitioned by the Government in February, 1918.

The average price of platinum per troy ounce in New York in 1914 was about \$45, whereas in 1918 it was \$105 (more than 5 times that of gold). In 1924 the price was \$125 per troy ounce, but in 1927 the price was less than \$100 per ounce, due, it is reported, to the extensive deposits recently discovered in the Transvaal.

712. Platinum Compounds. — When platinum is dissolved in aqua regia and the excess of nitric acid removed by evaporation, brownish-red crystals of **chloroplatinic acid**, $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, are obtained. When heated to 300° , this acid decomposes thus:

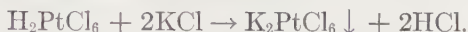


Platinous
chloride

When asbestos is soaked in a solution of H_2PtCl_6 , and then ignited, finely divided platinum is deposited on the fiber. The

product is known as **platinized asbestos**; it is an excellent catalyst.

When a solution of chloroplatinic acid is treated with a solution of a potassium salt, such as potassium chloride, a reddish-yellow crystalline precipitate of **potassium chloroplatinate** is obtained:

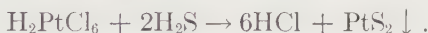


The salt is sparingly soluble in water, but practically insoluble in 75 per cent alcohol. Ammonium salts behave in a similar way, forming $(\text{NH}_4)_2\text{PtCl}_6$. The corresponding sodium salt is soluble, however, in dilute alcohol, and much more soluble in water.

Chloroplatinic acid is used as a reagent in separating potassium or ammonium from sodium. When $(\text{NH}_4)_2\text{PtCl}_6$ is heated, metallic (spongy) platinum is obtained (equation).

Platinic chloride, PtCl_4 , may be prepared by direct action of excess of chlorine on platinum. The salt decomposes above 500° . The pentahydrate, $\text{PtCl}_4 \cdot 5\text{H}_2\text{O}$, may be obtained as red crystals.

Platinic sulfide, PtS_2 , is obtained as a dark-brown precipitate by treating a cold solution of chloroplatinic acid with hydrogen sulfide:



The precipitate is soluble in aqua regia; also in alkali sulfides (see Stannic Sulfide).

Barium platinocyanide, $\text{BaPt}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$, is fluorescent when bombarded by X-rays; it is used therefore for X-ray screens.

Potassium chloroplatinite, K_2PtCl_4 , may be obtained as rose-red crystals by reducing K_2PtCl_6 . It is used in platinum printing in photography, being reduced to metallic platinum.

METALS ALLIED TO PLATINUM

713. Ruthenium, Ru. — *Ruthenium* (*Ruthenia*, Russia) was proved by Claus (1845) to be present in platinum ores from the Ural. The metal also is found in *iridosmine* (an alloy containing iridium and osmium). The production of the metal is small.

Ruthenium is a dark gray (or nearly black) hard, brittle, heavy metal. At high temperatures it is attacked by oxygen, thus showing a relationship to iron. The pure metal is very resistant to the action of acids, but combines with chlorine at a high temperature.

Ruthenium tetroxide, RuO_4 , is formed when the metal is heated in oxygen at $1,000^\circ$. This compound is yellow in color, melts at about 26° , and is volatile with steam.

714. Rhodium, Rh. — *Rhodium*, (Greek *rhodon*, a rose, from the rose-red color of its salts) was discovered by Wollaston in 1804. The metal has the appearance of aluminium, but is much heavier. It is very resistant to corrosion by acids, but is more readily attacked by free chlorine than are the other metals of the triad.

Chemical apparatus has been constructed of pure rhodium, as well as of an alloy of the metal (*rhodium*). It also is used in tipping gold pens and in electric pyrometers.

An alloy of rhodium and platinum constitutes the positive element of certain thermo-couples.

Our refiners reported the recovery of 326 troy ounces of rhodium in 1918. In 1920 the United States imported for consumption 2,053 ounces of rhodium.

715. Palladium, Pd. — *Palladium* (after *Pallas*, a new planet discovered in 1802) was discovered by Wollaston in 1804. The metal is contained in most platinum ores, and is often found alloyed with gold. It is obtained from platinum ores, as well as from the electrolytic muds which are obtained as by-products in the refining of certain ores of nickel.

Palladium resembles platinum and silver. Its density is 11.4 and its melting point is $1,555^{\circ}$, being the lowest of all the platinum metals.

Palladium adsorbs very large volumes of hydrogen, the amount under exceptional conditions being as high as 900 volumes. The adsorbed hydrogen is exceedingly active. Thus, a charged palladium electrode, when immersed in a solution of cupric sulfate, precipitates the copper readily (explain).

Palladium is more basic than the other elements of the platinum family. It dissolves in nitric acid, forming the nitrate $\text{Pd}(\text{NO}_3)_2$; it also forms the sulfate PdSO_4 . These salts are moderately stable.

Palladium is employed for the preparation of graduated surfaces for scientific instruments, for it has a silver-white color and does not tarnish. Gold-palladium alloy is used extensively in dentistry as a substitute for gold-platinum alloy. The metal also is employed as a catalyst: *e.g.*, for the hydrogenation of certain unsaturated carbon compounds (127); also, as a reducing agent (palladium-hydrogen electrode).

In 1915 refiners in the United States recovered 1,541 troy ounces of palladium, 4,779 ounces in 1917, and 4,309 ounces in 1920. In the year 1919, the United States imported for consumption 3,739 troy ounces of the metal, which rose to 6,944 ounces in 1920.

The average price per troy ounce of palladium was \$44 in 1914 and \$135 in 1918.

716. Osmium, Os. — *Osmium* (Greek, meaning *a smell*, because of the peculiar odor of its volatile oxide, OsO_4) was discovered by Tennant in 1803. He found it to be present in a metallic residue which is obtained when platinum ores are dissolved in aqua regia. Osmium is found in iridosmine or osmiridium (an alloy of osmium and iridium) and in native platinum. It is interesting in being the heaviest of known bodies (density, 22.5).

When finely divided, it oxidizes somewhat readily. Crystalline osmium resists the action even of aqua regia, but the amorphous metal dissolves in fuming nitric acid, and more slowly in aqua regia.

Osmium is chiefly acid-forming in character.

Osmium tetroxide, OsO_4 , is commonly called "osmic acid," although it does not play the rôle of an acid anhydride. It may be obtained by heating finely divided osmium in air to a temperature of about 400° , the osmium burning to form a highly poisonous vapor! Like the corresponding ruthenium compound, it is volatile with steam, the vapor having a very irritating and disagreeable smell, somewhat similar to that of chlorine. It is used in biology for staining and hardening tissues, the oxide being reduced to metallic osmium. It was formerly employed in manufacturing filaments for electric bulbs, but has been replaced by tungsten. Osmium forms a fluoride, OsF_8 , in which the metal has a maximum valence of eight.

In 1919 the United States imported for consumption 2,339 troy ounces of osmium, but the following year only 593 ounces were imported. 1,374 ounces of osmiridium were imported in 1919 and 4,473 in 1920.

717. Iridium, Ir. — *Iridium* (Greek or Latin, *iris*, a rainbow, from the varying tint of its salts) was discovered, along with osmium, by Tennant in 1803. It occurs in platinum ores, as the alloys are usually relatively rich in iridium. Being insoluble in aqua regia, they are left behind when platinum ores are treated with the solvent.

Iridium is a silver-white, hard and brittle metal. It has a density of 22.4 (nearly as heavy as osmium).

An alloy of iridium and osmium is used in producing tips for gold pens (*iridosmine*). It also is used for hardening platinum and for rendering it more resistant to corrosion. Platinum-iridium alloys are used extensively in electrical work. The *standard meter bar*, kept at the International Bureau of Weights and Measures at Sèvres, is an alloy of platinum and iridium.

In the year 1917, the United States imported for consumption 3,619 troy ounces of iridium, and 4,718 ounces in 1920. The average price per troy ounce in 1914 was \$65, while in 1918 it was \$175. The metal is more expensive than platinum or palladium.

718. Review and Supplementary. — The metals may be divided into light and heavy metals, the light ones having a density of less than five.

The most important light metals are: (1) the alkali metals; (2) the alkaline earth metals; (3) beryllium and magnesium; (4) aluminium.

Of the heavy metals, gold, silver, copper, tin, lead, and iron have been longest known, because they occur native, or can be easily prepared by reducing their ores.

Aluminium is the most abundant metal in the earth's crust, followed by iron, calcium, sodium, potassium, magnesium, and titanium. It is interesting to note that none of these has a high atomic weight or atomic number:

	<i>Atomic weight</i>	<i>Atomic number</i>
Al.....	26.97	13
Fe.....	55.84	26
Ca.....	40.07	20
Na.....	23	11
K.....	39.1	19
Mg.....	24.32	12
Ti.....	47.9	22

The densities of the metals range from 0.53 (Li) to 22.5 (Os), while their melting points range from -38.8° (Hg) to $3,400^{\circ}$ (W).

Gold and silver are the most malleable and ductile; and iron (steel), nickel, and copper possess the greatest tenacity. Silver, copper, and aluminium are excellent conductors; and iridium and chromium are hard enough to scratch glass.

The alkali and the alkaline earth metals are the most active or electropositive of the metals, which means that they have the greatest tendency to give up outer electrons to form positive ions. Thus: $M \rightarrow M^{+} + \ominus$.

Metals which resist corrosion, such as gold, platinum, and chromium, have much less tendency to part with outer or valence electrons.

The oxides and hydroxides of the active metals are strongly basic. Thus:



These oxides and hydroxides are more stable and soluble, as a rule, than are the corresponding compounds of other metals, particularly those of silver, gold, and platinum and allied metals.

Certain of the metals, particularly those of Groups III, IV, and V, are amphoteric in nature; that is, they are weakly basic as well as acidic: *e.g.*, aluminium, tin, and antimony. Their salts, therefore, are partially hydrolyzed by water.

In the scheme of qualitative analysis, the metals are divided into well-defined groups, which depend upon the use of group reagents, as shown in the outline given below.

DEFINITION OF THE GROUPS OF METALS

Group I. Silver Group. Metals precipitated as chlorides (lead only partially) by hydrochloric acid: Ag, Pb, Hg (ous). The precipitate may consist of: AgCl , PbCl_2 , Hg_2Cl_2 .

Group II. Copper-Tin Group. Metals precipitated by hydrogen sulfide in 0.3 *N* acid solution: Copper Sub-group: Hg (ic), Bi, Pb, Cu, Cd (sulfides insoluble in yellow ammonium sulfide); and Tin Sub-group: As, Sb, Sn (sulfides soluble in yellow ammonium sulfide).

The precipitate may consist of: HgS , Bi_2S_3 , PbS , CuS , CdS , As_2S_3 , As_2S_5 , Sb_2S_3 , Sb_2S_5 , SnS , SnS_2 .

Group III. Iron-Zinc Group. Metals not precipitated by hydrogen sulfide in acid solution, but precipitated by ammonium sulfide: Fe, Cr, Al, Ni, Co, Mn, Zn.

The precipitate may consist of: FeS , $\text{Cr}(\text{OH})_3$, $\text{Al}(\text{OH})_3$, NiS , CoS , MnS , ZnS .

Group IV. The Alkaline Earth Group. Metals not precipitated by sulfides, but precipitated by ammonium carbonate: Ba, Sr, Ca, (Mg).

The precipitate may consist of: BaCO_3 , SrCO_3 , CaCO_3 . (Mg is not precipitated when sufficient NH_4Cl is present.)

Group V. The Alkali Group. Metals not precipitated by any of the preceding reagents: K, Na, (NH_4) .

Note. — Magnesium is often classified as a member of the Alkaline Earth Group, but in actual analysis it falls into the Alkali Group; that is, it is not precipitated as a carbonate along with carbonates of barium, calcium and strontium, but passes into the last filtrate with K^+ , Na^+ , and $(\text{NH}_4)^+$.

SEPARATION OF THE METALS INTO GROUPS.
OUTLINE OF THE PROCESS

Solution containing all common metals: add slight excess of 6 N HCl

<i>Precipitate:</i>	<i>Filtrate (Acidity 0.3 N): saturate cold with H₂S</i>				
AgCl, PbCl ₂ , Hg ₂ Cl ₂ (BiOCl, SbOCl) Extract with dil. HCl upon fil- ter. Residue: AgCl, PbCl ₂ , Hg ₂ Cl ₂ .	Precipitate: HgS, PbS, CuS, Bi ₂ S ₃ , CdS, As ₂ S ₃ , (As ₂ S ₅), Sb ₂ S ₃ , SnS, SnS ₂ ; Sulfur Treat with (NH ₄) ₂ Sx.		<i>Filtrate:</i> Add NH ₄ Cl, NH ₄ OH, and (NH ₄) ₂ S.		
	<i>Residue:</i> Copper Sub-Group HgS, PbS, CuS, Bi ₂ S ₃ , CdS.	<i>Extract:</i> Tin Sub-Group (NH ₄) ₃ AsS ₄ , (NH ₄) ₃ SbS ₄ , (NH ₄) ₂ SnS ₃ . Add HCl.	Precipitate: CoS, NiS, FeS, ZnS, MnS, Al(OH) ₃ , Cr(OH) ₃	<i>Filtrate:</i> Add (NH ₄) ₂ CO ₃ .	
		<i>Precipitate:</i> As ₂ S ₅ , Sb ₂ S ₅ , SnS ₂ , Sulfur.		<i>Precipitate:</i> CaCO ₃ , SrCO ₃ , BaCO ₃ .	<i>Filtrate:</i> Salts of Mg, K, and Na.

EXERCISES

- Outline the chief properties and relations of the Platinum Metals. Write the formulae of some of their compounds (*e.g.*, oxides and chlorides).
- Tell all you can about the occurrence and production of platinum. How is the metal prepared in the form of "spongy platinum," and how is it obtained in the massive state?
- State as fully as you can the properties of platinum. What precautions should be observed in the use of chemical ware constructed of the metal?
- State the most important uses of platinum, pointing out its relation to the chemical industries. What effect did the World War have upon the production and price of platinum? Explain.
- Show, including equations, how you could prepare the following compounds: (1) H₂PtCl₆·6H₂O; (2) K₂PtCl₆; (3) (NH₄)₂PtCl₆; (4) K₂PtCl₄; and (5) PtS₂. State briefly the properties and uses of these compounds. What ions are formed when Na₂PtCl₆ is dissolved in water?
- How could you prepare "platinum black" and "platinized asbestos"? For what are they used? What do you know about platinum as a catalyst?
- State the properties and uses of palladium.
- Outline the properties and uses of rhodium. To what does the element owe its name?
- State what you know about the metals, ruthenium and osmium. Why were they so named? Compare the tetroxides of the two elements.

For what is "osmic acid" used? What precaution must be observed in handling the substance?

10. Give the occurrence, properties, and chief uses of iridium. Why was the element so named? What is osmiridium?

11. Compare and contrast gold and its compounds with platinum and its compounds. Why should not gold be placed in Group VIII of the Periodic Table?

12. Four grams of a mixture containing ammonium chloride were treated with water until all the chloride was dissolved. The solution was then treated with an excess of chloroplatinic acid, and the carefully purified and dried precipitate yielded 0.600 g. of pure spongy platinum upon ignition. Basing your calculation upon these data, what percentage of NH_4Cl did the mixture contain? How much AgNO_3 would be required to precipitate the chlorine contained in the ammonium chloride?

13. Compare and contrast the metals of the iron group with those of the platinum group.

14. Explain the use of platinum in photography.

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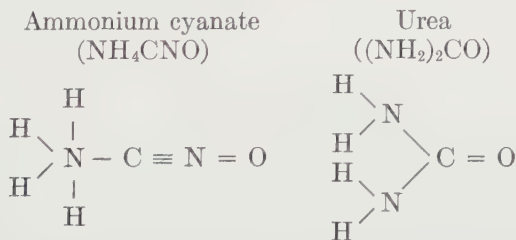
PART IV

SUPPLEMENTARY: CARBON COMPOUNDS

CHAPTER XL

ORGANIC CHEMISTRY. HYDROCARBONS. FUEL AND FLAME

719. **Meaning of Organic Chemistry.** — Organic Chemistry treats of the carbon compounds, which now number over 230,000, whilst the combined number of all other compounds is about 25,000. The laws of organic chemistry do not differ from those of inorganic chemistry. A century ago it was thought that carbon compounds found in organized bodies — plants and animals — were formed only as the result of a “vital force,” and could not be synthesized, therefore, by man. This notion was disproved in 1828, as previously stated, by the German chemist, F. Wöhler, who obtained urea, a nitrogenous waste material of the body, by warming ammonium cyanate, a compound capable of synthesis from inorganic substances. Both compounds have the same formula ($\text{N}_2\text{H}_4\text{CO}$) and identical molecular weight. The transformation of ammonium cyanate into urea was of much interest, for it was the first time an organic compound was prepared without the aid of life processes. Ammonium cyanate and urea are *isomers* (Greek *isos*, equal + *meros*, part), but their properties are different, owing to the different arrangement of the atoms constituting the molecule of each. This may be shown as follows:



Since the synthesis of urea, innumerable other carbon compounds have been synthesized in the laboratory, so there is no barrier between organic and inorganic chemistry: one set of laws governs both these branches of chemistry. The name “Organic Chemistry” is allocated to the Chemistry of the Carbon Compounds.

720. Sources of Carbon Compounds. — Organic compounds, such as the sugars, starch, cellulose, certain oils, and alkaloids (quinine, strychnine, nicotine, caffeine, etc.), occur abundantly in plants. Other carbon compounds, such as fats and oils, are furnished abundantly by animals. Many carbon compounds also are found in petroleum. Still other carbon compounds are obtained by the destructive distillation of coal or wood: *e.g.*, benzene, toluene, carbolic acid, naphthalene, wood alcohol, acetic acid, acetone, and methane. From these fundamental substances thousands of other carbon compounds, such as the dyes, may be prepared.

721. Classification of Carbon Compounds. — The organic compounds are usually divided into two classes —

- (I) **Fatty or Aliphatic Compounds** (Greek, meaning *fat*); and
- (II) **Cyclic or Ring Compounds.**

Animal and vegetable fats are included in the first class of compounds. Since the carbon atoms of the molecules of fatty compounds are arranged in a chain or row, they are also termed "chain compounds." The aliphatic compounds are often defined as those derived from the hydrocarbon methane, CH_4 .

The second class of compounds have molecules in which the carbon atoms are arranged in a closed chain or ring, which explains the origin of the name "cyclic" or "ring."

Most carbon compounds contain only a very small number of elements, the principal ones being carbon, hydrogen, oxygen, and nitrogen, — all being elements present in the atmosphere (N_2 , O_2 , H_2O , CO_2).

HYDROCARBONS

(Compounds of Hydrogen and Carbon)

722. Sources of Hydrocarbons. — Hydrocarbons are compounds of hydrogen and carbon only: *e.g.*, methane (marsh gas) CH_4 , acetylene C_2H_2 , and benzene C_6H_6 . Hydrocarbons occur as gases, liquids, and solids, several hundred of them being known.

Natural gas is chiefly methane, and petroleum is composed almost entirely of a mixture of hydrocarbons. By the destructive distillation of coal, important hydrocarbons are found in the gaseous product; and the coal-tar is a source of benzene, toluene, naphthalene (moth-balls), and other hydrocarbons. Likewise, when wood is heated in closed vessels hydrocarbons, as well as other

substances, are formed. Turpentine and rubber (caoutchouc) are hydrocarbons.

723. Homologous Series. — As carbon compounds are exceedingly numerous, it simplifies their study to arrange them in families, the classification being based on composition and properties. Thus, the hydrocarbons have been divided into families which are called **homologous** (Greek, *corresponding*) **series**. Each member of an homologous series differs from the member which precedes or follows it by one atom of carbon and two atoms of hydrogen, or by CH_2 . *Members of the same family, or homologous series, have the same general formula and similar chemical properties, as shown by the table below.*

HOMOLOGOUS SERIES OF HYDROCARBONS

(I)	(II)	(III)
Methane (Paraffin) Series	Ethylene Series (or Olefines)	Acetylene Series
General formula: $\text{C}_n\text{H}_{2n+2}$	General formula: C_nH_{2n}	General formula: $\text{C}_n\text{H}_{2n-2}$
CH_4 , Methane.....
C_2H_6 , Ethane.....	C_2H_4 , Ethylene.....	C_2H_2 , Acetylene
C_3H_8 , Propane.....	C_3H_6 , Propylene.....	C_3H_4 , Allylene
C_4H_{10} , Butane.....	C_4H_8 , Butylene.....	C_4H_6 , Crotonylene
C_5H_{12} , Pentane.....	Etc.....	Etc.....

The *paraffins* are called *saturated hydrocarbons*, for the carbon atom has all its four valences employed. There are other homologous series of hydrocarbons, such as the benzene series, of which benzene (C_6H_6) is the first member. The members of this series have the general formula $\text{C}_n\text{H}_{2n-6}$. The second member of the series is toluene, C_7H_8 .

THE METHANE SERIES (OR PARAFFINS); SATURATED COMPOUNDS

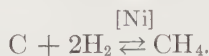
724. Methane or Marsh Gas, CH_4 . — This is the only hydrocarbon the molecule of which contains only one atom of carbon. The compound is called “marsh gas” because it is formed in marshes or pools, formed by the decay of vegetable matter. It also is frequently present in coal mines, being the dreaded *fire-damp* of the miner. Natural gas is largely methane. When wood or coal is subjected to destructive distillation, large quantities of this gas are produced, coal gas containing ordinarily from 35 to 40 per cent by volume.

Methane is usually prepared in the laboratory by strongly heating a mixture of anhydrous sodium acetate and sodium hydroxide or soda-lime:



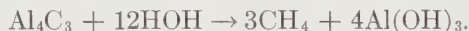
The gas may be collected over water. Methane thus prepared is contaminated with ethylene and hydrogen.

Methane can be synthesized by different methods. For example, by passing hydrogen through a heated tube containing nickel (catalyst) mixed with specially prepared carbon:

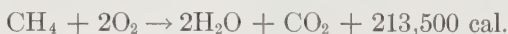


At 475° and standard pressure, equilibrium is attained with 51 per cent of CH₄.

Methane also may be prepared by the hydrolysis of aluminium carbide:



Methane is a colorless, odorless, tasteless gas, and only slightly soluble in water. Under normal atmospheric pressure and at -165°, it forms a colorless liquid. Methane, like other paraffins (Lat. *parum*, little + *affinis*, affinity), is indifferent to most chemical reagents. *All hydrocarbons burn, forming water and carbon dioxide.* Methane burns with a pale bluish flame and with the formation of much heat:



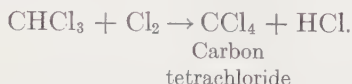
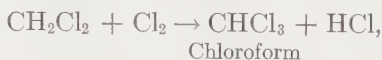
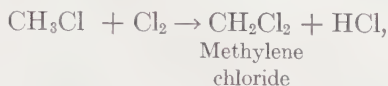
A mixture of methane and oxygen (or air) is extremely explosive, the maximum effect being obtained when 2 volumes of oxygen or 10 volumes of air are mixed with 1 volume of methane.

Chlorine and bromine, but not iodine, interact with the paraffins and the change is promoted by light. Thus, when equal volumes of methane and chlorine are exposed to diffused sunlight, they gradually interact to form *methyl chloride*, CH₃Cl, and HCl:



This type of chemical change is called **substitution**, for chlorine is substituted atom for atom for hydrogen. (How does *substitution* differ from *displacement*?)

By the addition of more chlorine, other substitution products may be gradually formed:



When a mixture of methane and chlorine is exposed to direct sunlight, an explosion occurs:



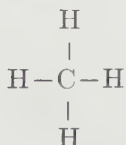
The paraffins are called **saturated compounds**, for they do not form addition products (728).

The melting and boiling points of the lower hydrocarbons of the methane series are given below.

Formula	Name	Melting Point	Boiling Point
CH_4	Methane	-186°	-165°
C_2H_6	Ethane	-172°	-93°
C_3H_8	Propane	-45°
C_4H_{10}	Butane	-135°	-0.1°
C_5H_{12}	Pentane	-130.8°	36.3°
C_6H_{14}	Hexane	-94°	68.9°
C_7H_{16}	Heptane	-94.5°	98.4°
C_8H_{18}	Octane	-57.4°	125.6°

The hydrocarbons $\text{C}_n\text{H}_{2n+2}$ are distinguished by the suffix "ane."

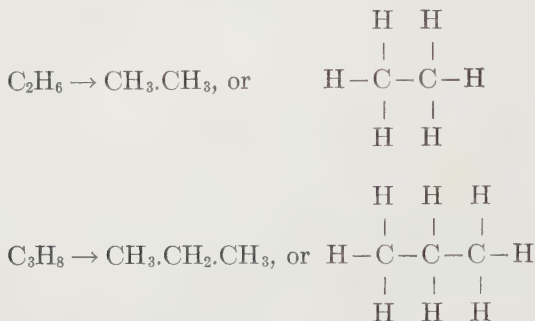
725. Graphic or Structural Formulae of the Paraffins. — The explanation of the structure of the paraffins is based upon the theories (1) *that the carbon atom is quadrivalent*, and (2) *that the atoms of carbon cannot only combine with atoms of other elements, but are capable of uniting with one another in a chain*. Thus, the graphic formula of methane may be written as follows:



Chemists believe that the carbon atom of the methane molecule is situated at the center of a tetrahedron, with the four hydrogen atoms at the corners (see the Diamond, 422).

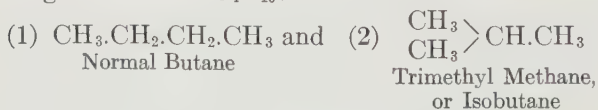
In case of the chlorine substitution products, chlorine atoms may be substituted for an equal number of hydrogen atoms: *e.g.*, methane and carbon tetrachloride have similar structures.

The graphic formulae of ethane (C_2H_6) and propane (C_3H_8) may be written thus:

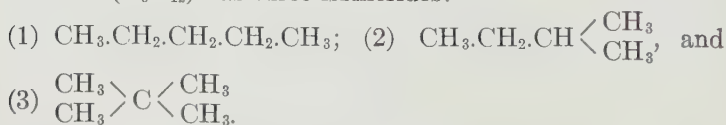


Such compounds are called "straight-chain" compounds.

We have seen that ammonium cyanate and urea are isomers or isomerides (719). The phenomenon of isomerism is very common in organic chemistry. **Isomers** are compounds containing the same elements in the same proportions by weight, but they show marked differences in properties, because the architecture of their molecules is different. No isomers of CH_4 , C_2H_6 , or C_3H_8 are known; but there are two compounds or isomerides having the formula C_4H_{10} :



Pentane (C_5H_{12}) has three isomerides:



Five compounds with the formula C_6H_{14} are known, and there are 802 possible isomerides of $C_{13}H_{28}$, but chemists have not attempted to prepare all of them.

726. Organic Radicals. — There are many groups of atoms containing carbon which pass unaltered from compound to compound. Such groups have a definite valence and are called *organic radicals*. The following radicals and compounds containing them may serve as illustrations:

<i>Radical</i>	<i>Chloride</i>	<i>Hydroxide</i>
CH ₃ , Methyl	CH ₃ Cl, Methyl chloride	CH ₃ OH, Methyl hydroxide (Methyl alcohol)
C ₂ H ₅ , Ethyl	C ₂ H ₅ Cl, Ethyl chloride	C ₂ H ₅ OH, Ethyl hydroxide (Ethyl alcohol)
C ₃ H ₇ , Propyl	C ₃ H ₇ Cl, Propyl chloride	C ₃ H ₇ OH, Propyl hydroxide (Propyl alcohol)
C ₃ H ₅ , Glyceryl	C ₃ H ₅ Cl ₃ , Glyceryl chloride	C ₃ H ₅ (OH) ₃ , Glyceryl hydroxide (Glycerol)

The radical may be derived from the corresponding hydrocarbon by withdrawing one atom of hydrogen. It should be noted, however, that these radicals are not names of substances.

727. Mineral Oils. — **Petroleum** (Lat. *petra*, rock + *oleum*, oil), or "rock oil," consists principally of a mixture of hydrocarbons. It occurs largely in California, in Oklahoma, and in other states; also in Russia, Mexico, the Dutch East Indies, Galicia, Persia, and Rumania. In 1921, the United States produced nearly 470,000,000 barrels of 42 gallons each, while the world's production was 760,000,000 barrels. In 1925, the world's production of crude petroleum rose to 1,066,220,000 barrels, of which the United States supplied 71.6 per cent.

In 1926 the domestic production was 770,874,000 barrels, 84 per cent of which was from Midcontinent and California fields.

In 1927 the world's production was 1,261,083,000 barrels, of which the United States furnished 71 per cent.

Oil is trapped in what the geologist calls an *anticline*, a sort of inverted bowl of clay or shale, and is reached by drilling wells. Colonel Drake dug the first petroleum well at Titusville, Pennsylvania, in 1859.

Russian petroleum occurs in and around Baku in the region of the Caspian Sea. As early as 600 B.C. the "eternal fires of Baku" attracted the fire-worshippers. The origin of petroleum is not known.

Petroleum is separated into various products by **fractional distillation**. This means that the components of petroleum have different boiling points, and may therefore be separated by distillation, the receiver of the still being changed from time to time.

Petroleum contains in solution gases, such as methane (CH_4) and ethane (C_2H_6). When the liquid is gently heated these gases are given off and are utilized as fuel and for the production of carbon-black (427). As the temperature is slowly raised heavier hydrocarbons are vaporized. After the separation of the true gases, the next product is the light liquids which are usually called **naphthas**. These consist largely of pentane (C_5H_{12}) and hexane (C_6H_{14}). This fraction is used as a solvent in the rubber and varnish industries. The next fraction is **gasoline**, which contains hydrocarbons having from six to ten carbon atoms in the molecule ($\text{C}_6\text{H}_{14} - \text{C}_{10}\text{H}_{22}$). It is employed extensively as motor fuel and as a solvent. The temperature of the still is now approximately 200° and it gradually rises to about 375° , **kerosene** being obtained. In this fraction there are molecules containing from ten to fifteen carbon atoms ($\text{C}_{10}\text{H}_{22} - \text{C}_{15}\text{H}_{34}$). Kerosene is an excellent illuminant and fuel. Other fractions obtained are **middle fractions** and **light** and **heavy paraffin distillates**. The middle fractions are "cracked" to form gasoline. The paraffin distillates yield **lubricating oil** and **paraffin**. The solid members of the series ($\text{C}_{22}\text{H}_{46}$ to $\text{C}_{28}\text{H}_{58}$) crystallize in flakes. **Vaseline** contains the hydrocarbons $\text{C}_{22}\text{H}_{46}$ and $\text{C}_{23}\text{H}_{48}$. The tarry residue in the still is employed as artificial asphalt and as a source of a light, porous **coke**.

According to G. L. Wendt, Midcontinent petroleum will furnish about 4 per cent of gas, 25 per cent of naphthas and gasoline, 15 per cent of kerosene, 40 per cent of gas oil, 12 per cent of paraffin and lubricating oils, and 4 per cent of coke. Before use, the gasoline, kerosene, and paraffin distillates must be refined.

Gasoline is the most prized derivative of petroleum. Since the greatly increased demand for gasoline, chemists have been busy with the problem of increasing the yield. Immense quantities of gasoline have been produced by "cracking" processes which have been invented within recent years. The crude petroleum is first separated into fractions by the ordinary distillation methods, and then the middle fractions, which have a relatively low fuel value, are heated or distilled at very high temperature and pressure, whereby the heavier molecules break down to yield hydrocarbons of lower molecular weights. When the crude oil is heated in cracking coils at a pressure of from 350 to 600 pounds, it may yield as much as three times the amount of gasoline as would be obtained under ordinary distillation. By the cracking process one barrel of crude petroleum ordinarily yields almost as much gasoline as

was previously obtained from two. In 1924, the ratio of cracked gasoline to the primary distillation, or straight gasoline, was one barrel to three and two-thirds.

Of the 9,000,000,000 barrels of oil produced in the United States up to June 30, 1926, about 3,000,000,000 barrels were produced in the last five years. The consumption of oil in the United States is about 70 per cent of the world's supply.

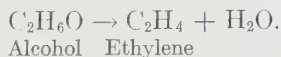
We have vast deposits of the rock called **oil shale**. It is reported that the state of Indiana has over 450 trillion tons of the rock, and there are whole mountains of it in Colorado and in Utah. When heated in appropriate stills these shales yield from 10 to 50 gallons of oil per ton; but at present the expense of production is too high to compete with petroleum. In the future, however, they will be, no doubt, of great value. Furthermore, there are relatively few cases in which coal cannot satisfactorily be substituted for fuel oil. Then, too, colloidal fuel will materially aid in relieving the diminishing stores of petroleum, and will also lead to the utilization of coal waste and inferior fuels. Synthetic fuel can now be produced.

According to W. E. Treat, coal may be pulverized to the consistency of talcum powder; when heated, it flows like water, giving virtually a liquid fuel.

Dr. F. Bergius and other European scientists have perfected a process for the transformation of coal into oil. The essential principle of the process consists in chemically combining hydrogen gas with coal by means of high temperature and pressure. A complex mixture of gaseous, liquid, and solid compounds is produced, and these compounds are similar to the hydrocarbons obtained from natural wells.

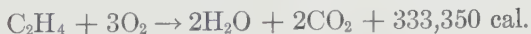
UNSATURATED HYDROCARBONS

728. Ethylene (Olefiant Gas), C_2H_4 . — Ethylene is an important hydrocarbon gas, being the first member of an homologous series of compounds called the **ethylene** or **olefiant-gas series**. The gas may be produced by abstracting the elements of water from ethyl alcohol. This may be accomplished by heating alcohol with sulfuric or phosphoric acid, or by passing the vapor of alcohol over kaolin (a catalyst) at a high temperature:

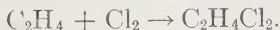


For laboratory use, the gas can be conveniently prepared by allowing alcohol slowly to flow into syrupy phosphoric acid at a temperature of 200° to 220° .

Ethylene is a colorless gas with an ethereal odor. It is more easily liquefied than methane and is more soluble in water. The gas burns with a very luminous flame:

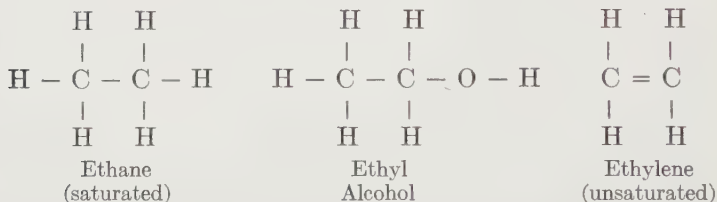


It is extremely explosive when mixed with air or oxygen. Unlike methane, it combines directly with chlorine and bromine to form *addition products*. Thus, it unites with chlorine to form ethylene chloride, $C_2H_4Cl_2$, an oily liquid, long known as "Dutch liquid":

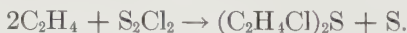


Since ethylene forms addition compounds, it is called an unsaturated compound. *Unsaturated compounds have the property of decolorizing a solution of bromine.*

The relation of ethylene to ethane and alcohol is shown by the following graphic formulae:



Ethylene is an important illuminant. During the Great War the United States used large quantities of the compound in the manufacture of "mustard gas," $(C_2H_4Cl)_2S$:



"Mustard gas" is really a liquid, boiling at 219° . It was first employed in warfare by the Germans at Ypres, July 20, 1917.

Ethylene is an excellent anesthetic. In using the gas it must be borne in mind that it mixes with air to form a powerful explosive.

It is an interesting fact, discovered a few years ago, that when carnations were shipped to Chicago, the flowers went to sleep, or closed up. It was demonstrated that this was caused by ethylene. Experiments were then made on dogs, followed by experiments on man.

Ethylene is very useful in cutting and welding metals and for coloring green citrus fruit yellow.

729. Acetylene, C_2H_2 .—Acetylene can be prepared very easily by treating calcium carbide, CaC_2 , with water:



(What type of chemical reaction does this illustrate?) The gas may be collected over water.

Acetylene may be formed synthetically by producing an electric arc between carbon electrodes in an atmosphere of hydrogen; it also is formed when coal gas undergoes incomplete combustion.

Acetylene is a colorless gas, which, when pure, has an ethereal odor. The impure gas, however, usually has a disagreeable odor. It is slightly soluble in water and is somewhat poisonous. Acetylene burns with an intensely luminous flame:



It is dangerously explosive when mixed with air or oxygen, and the range of explosive mixtures is great. Like ethylene, it readily forms addition products, such as acetylene tetrachloride, $\text{C}_2\text{H}_2\text{Cl}_4$, and the tetrabromide, $\text{C}_2\text{H}_2\text{Br}_4$. Acetylene is therefore an unsaturated compound. Its graphic formula may be written thus:



Acetylene and certain metals form compounds known as **acetylides**: e.g., *copper acetylide*, $\text{Cu}_2\text{C}_2\cdot\text{H}_2\text{O}$, and *silver acetylide*, $\text{Ag}_2\text{C}_2\cdot\text{H}_2\text{O}$. These two compounds are explosive.

Acetylene is an endothermic compound:



Like other endothermic substances, it is not very stable; it may be exploded by shock. This explains why it is unsafe to compress acetylene in supply cylinders. The gas, however, may be safely dissolved under pressure in acetone ("Prestolite").

Acetylene is used extensively as an illuminant, for which a special burner with a very fine hole is required. The oxyacetylene torch (blowpipe) is exceedingly hot (nearly $3,500^\circ \text{C.}$), being utilized in cutting and welding metals (Fig. 199).



Courtesy, The Linde Air Products Co.

FIG. 199. Welding a Pipe Line.

FUEL; ILLUMINATING GASES

730. Natural Gas. — Natural gas occurs in certain localities, particularly in West Virginia, Oklahoma, Pennsylvania, Ohio,

California, Louisiana, Kansas, and Texas. It has accumulated under great pressure in the earth's crust, and is reached by borings. Natural gas contains from 80 to 95 per cent of methane, the average for the West Virginia and Pennsylvania gas being about 81 per cent, and for the Ohio, Indiana, and Kansas gases 93.6.

In 1917 the United States produced and consumed 795,110,376,000 cu. ft. of natural gas valued at over \$142,000,000. 62 per cent of the total production was consumed by industrial establishments. In 1926, the value of the gas produced was about \$294,000,000. In 1927 the production was nearly double that of 1917.

731. Coal Gas. — Large quantities of coal gas are produced by the destructive distillation of coal at high temperatures. **Coke, tar, and ammonia** are the **by-products**. Bituminous coal is heated to high temperatures in retorts (Fig. 200), from which a pipe leads

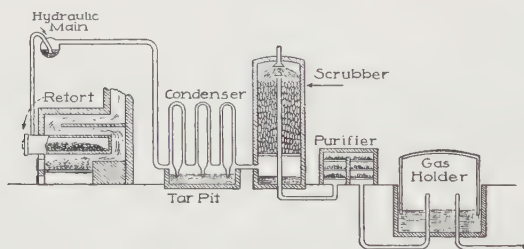


FIG. 200.

to the **hydraulic main**, where tar and water are condensed. The excess of tar flows into a **tar pit**. The hot gases and vapors are next passed through a series of pipes called **condensers**, to condense more tar and to cool the gas for further purification. The liquids collected in the tar pit separate into two layers — the lower being coal tar and the upper gas liquor (an aqueous solution of ammonia and ammonium compounds). The cooled gas is passed from the condensers to the **scrubber**, where ammonia is dissolved by water. The gas passes from the scrubber to the **purifiers**, where hydrogen sulfide is taken out by hydrated ferric oxide or lime. From the purifiers the gas passes to the **holder**, where it is stored over water and piped to the consumer.

A ton of coal yields, on the average, about 12,000 cu. ft. of gas, largely hydrogen and methane; it also contains considerable quantities of carbon monoxide and unsaturated hydrocarbons. There are also produced from 1,200 to 1,400 pounds of coke, about

120 pounds of tar, and ammonia liquor enough to produce from 7 to 25 pounds of ammonium sulfate.

It is of interest to note that *the destructive distillation of wood yields products somewhat similar to those obtained from coal: e.g., wood gas, a liquid distillate, wood tar, and charcoal.* The principal products obtained from wood are —

Charcoal (largely carbon),
Acetic acid ($\text{H.C}_2\text{H}_3\text{O}_2$),
Wood alcohol (CH_3OH),
Acetone ($(\text{CH}_3)_2\text{CO}$),
Wood tar.

The destructive distillation of wood was practiced in prehistoric times.

732. Oil Gas and Water Gas. — Petroleum distillates containing heavy hydrocarbons may be “cracked” into simpler hydrocarbons by heating. The products obtained are used as fuel and as illuminating gas: *e.g.*, “**Pintsch gas**” and “**Blau gas.**” Oil gases compressed into cylinders have been utilized in lighting railway trains. These gases are richer in illuminants than are ordinary gases. Blau gas was used to drive the engines of the dirigible *Graf Zeppelin*, which crossed the Atlantic Ocean in October, 1928.

We have seen that water gas is produced by passing steam through a bed of burning coke or anthracite coal:



The reaction takes place at a temperature of about $1,000^\circ$, but in the course of a few minutes the temperature drops, so that the steam must be turned off and the fuel burned with a forced draft until it is nearly white-hot. The process is then reversed. The production of water gas is therefore intermittent.

Water gas burns, producing a great deal of heat, but very little light unless in connection with Welsbach mantles. The gas is used largely for cooking and lighting. To increase its luminosity, it may be mixed with unsaturated hydrocarbons, such as ethylene and benzene. Oil gases are well adapted to this use. Water gas thus treated is called “carbureted water gas” (Fig. 201).

Since water gas contains a high percentage of carbon monoxide, it is much more poisonous than coal gas.

733. Producer Gas. — We have seen (438) that producer gas is manufactured when coal burns under such conditions as to yield

a large quantity of carbon monoxide (Fig. 202). As producer gas contains nitrogen (from the air), it has low heating value, but the cost of production also is low.

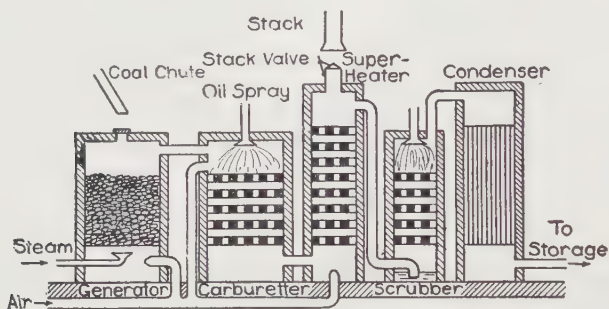


FIG. 201.

When air and steam together are forced through beds of hot coal, a *fuel gas* containing hydrogen, as well as carbon monoxide and nitrogen, is obtained. These gases can be made from a low-grade

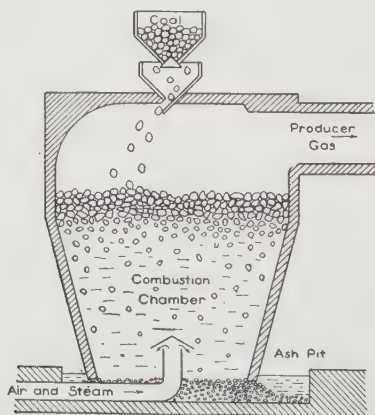


FIG. 202.

coal, even lignite. They give a uniform heat and require no stoking, and are extensively utilized for running gas-engines and in connection with a large number of metallurgical operations.

A kind of producer gas, called *blast furnace gas*, is formed in the reduction of iron ore; it is taken from the top of the blast furnace and is utilized to operate the gas-engines.

734. **Composition of Gases.** — The following table gives the composition of certain gases by volume:

COMPOSITION OF GASES BY VOLUME

	Pittsburgh Natural Gas	Coal Gas	Water	Carbur- eted Water Gas	Producer Gas
Hydrogen, H_2	0.0	46.0	52.88	37.96	8.6
Methane, CH_4	87.1	32.4	2.16	7.09	2.0
Other hydrocarbons...	11.5	3.4	13.41	0.4
Carbon monoxide, CO.....	8.6	36.80	32.25	24.4
Carbon dioxide, CO_2	1.6	3.47	4.73	5.2
Nitrogen, N_2	1.4	7.6	4.69	3.96	59.3
Oxygen, O_2	0.4	0.60	0.1

735. **Calorific Power of Fuels.** — The following table gives the calorific power of a number of gases and of solid fuels. The calorific value of fuel is of great importance to the chemical engineer. The heat is expressed in the British Thermal Unit (B.T.U.). (Re-read Section 106.)

CALORIFIC POWER OF FUELS IN BRITISH THERMAL UNITS (B.T.U.)

	<i>B.T.U. per cubic foot</i>	
Hydrogen.....	343	
Methane.....	1,064	
Acetylene.....	1,556	
Carbon monoxide.....	341	
Coal gas.....	600	} Approximate values
Water gas.....	300	
Carbureted water gas.....	600	
Producer gas (from coal or coke).....	140	
Blast furnace gas.....	100	
	<i>B.T.U. per lb.</i>	
Wood.....	8,000–9,000	
Peat (Theoretically dry).....	6,500–9,500	
Lignite.....	9,000–14,000	
Bituminous coal.....	14,600–15,050	
Anthracite.....	14,500–15,800	
Coke.....	14,000	
Fuel Oil.....	20,000	

CYCLIC COMPOUNDS

736. **The Aromatic Compounds.** — The cyclic compounds are exceedingly numerous, and many of them are very important. These substances have closed chains and are characterized by

great stability toward chemical reagents. In many respects their properties differ from those of the aliphatic compounds. One class of cyclic compounds is called the Aromatic Compounds, or benzene (C_6H_6) derivatives. Benzene may be regarded as the starting point in the preparation of closed-chain compounds, just as we regard methane as the fundamental compound in building up aliphatic or straight-chain compounds. Cyclic compounds are obtained on a large scale from coal tar, a thick, black liquid possessing a characteristic odor. It owes its color to suspended particles of carbon. The tar is a complex mixture, which contains neutral, acidic, and basic components. The neutral components are chiefly hydrocarbons of the aromatic series. Tar contains from 5 to 10 per cent of naphthalene and from 1 to 1.5 per cent of a mixture of benzene and toluene. Phenol, or carbolic acid, is the principal acidic component. The basic components are not present in large amount, the chief one being pyridine (C_5H_5N), a liquid with a disagreeable odor; it is used for denaturing alcohol.

Tar, like petroleum (727), is separated into components by **fractional distillation**, which is conducted in large iron stills or retorts, the vapors being condensed in long metallic worms immersed in cold water. The resulting liquid distillate is collected in four fractions, as shown below.

FRACTIONS FROM COAL TAR

Fraction	Temperature	Density
I. Light Oil, or Crude Naphtha.....	80°–170°	0.910–0.950
II. Middle Oil, or Carbolic Oil.....	170°–230°	1.01
III. Heavy Oil, or Creosote Oil.....	230°–270°	1.04
IV. Anthracene Oil, or Green Oil.....	Above 270°	1.10
V. Pitch.....		

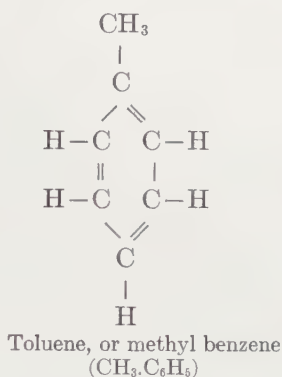
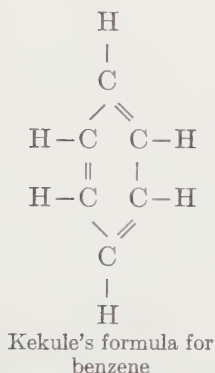
The light oil is separated into its components by further fractionation and then purified, partly by chemical means. The principal substances derived therefrom are benzene and its homologues, toluene and xylene:


Benzene.....	C_6H_6
Toluene, or Methyl Benzene.....	C_7H_8 , or $C_6H_5.CH_3$
Xylene, or Dimethyl Benzene.....	C_8H_{10} , or $C_6H_4(CH_3)_2$.

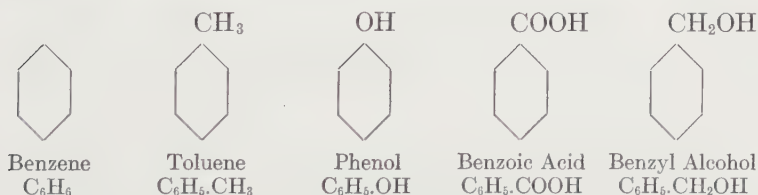
These belong to the homologous series having the general formula C_nH_{2n-6} .

The properties of benzene and of its derivatives are best explained

by assuming that the six carbon atoms of the compound are joined together in a ring. The structural formulae of benzene and toluene may be written thus:



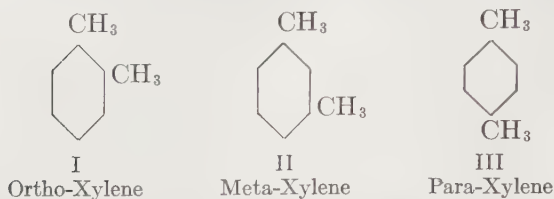
Organic chemists usually represent the benzene molecule by the symbol . By substituting atoms or radicals for hydrogen of benzene, the composition of the derivatives may be represented thus:



Xylene, or dimethyl benzene, $\text{C}_6\text{H}_4(\text{CH}_3)_2$, has two side-chains or radicals attached to the benzene nucleus and the position of these groups has an influence on the properties of xylene. In other words, isomeric forms of xylene are known. It is customary to number the carbon atoms in the benzene nucleus as follows:



Three isomeric xylenes are possible and all are known; they may be represented thus:

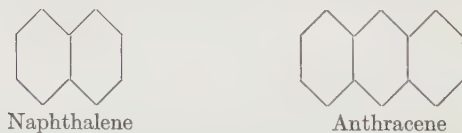


When the substitution products of benzene have the substituent atoms, groups, or side-chains, on adjacent carbon atoms (formula I), they are called **ortho-compounds**, and the substituent atoms or groups are said to be in the ortho- or 1:2-position. **Meta-compounds** are represented by formula II, the substituent atoms or groups occupying the 1 : 3-position; while the **para-compounds** are represented by formula III, in which the atoms or groups are in the 1 : 4-position.

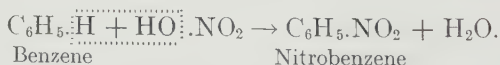
O-xylene boils at 142°, m-xylene at 139°, and p-xylene at 138°.

Benzene (Faraday, 1825) is a colorless, mobile liquid, having an aromatic odor. It boils at 80°, its specific gravity is 0.88 at 20°, and it is insoluble in water. Benzene is a solvent for fats, resins, phosphorus, etc. It burns with a luminous, smoky flame.

Naphthalene ($C_{10}H_8$) is assumed to contain two condensed benzene nuclei, while **anthracene** ($C_{14}H_{10}$) contains three:



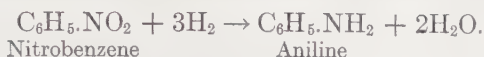
Aromatic compounds, unlike aliphatic compounds, may be readily nitrated, forming nitro-derivatives (389). Nitration is carried out by bringing the substance, *e.g.*, benzene or toluene, in contact with a mixture of concentrated nitric and sulfuric acids:



Nitrobenzene is a yellowish liquid, possessing an odor like that of bitter almonds. It is a poisonous compound, inhalation of its vapor being dangerous. It is prepared on a large scale for use in perfumery and for the production of aniline, the basis of innumerable dyes.

Aniline, or **aminobenzene** ($C_6H_5 \cdot NH_2$), was first obtained in 1826 by the distillation of indigo (Portuguese *anil*, indigo plant). It

is prepared by reducing nitrobenzene by means of hydrogen:

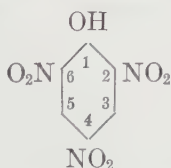


The hydrogen is formed by mixing iron filings and hydrochloric acid; these are added to the nitrobenzene.

Aniline is a poisonous, colorless oil, which gradually turns yellow when exposed to air, becoming ultimately nearly black. While aniline is neutral to litmus, it is basic with respect to acids and forms soluble salts, such as aniline hydrochloride, $\text{C}_6\text{H}_5.\text{NH}_2.\text{HCl}$. Aniline is not a dye. Great quantities of aniline are employed in the production of dyes, as well as other compounds.

From *coal tar* 10 "crudes" (benzene, toluene, naphthalene, anthracene, carbolic acid, etc.) are obtained, and from these about 300 "intermediates" are produced, and from the intermediates about 900 dyes, which yield about 5,000 brands.

737. Dyes and Dyeing. — **Picric** (Greek, meaning *bitter*) **acid**, or **trinitrophenol** ($\text{C}_6\text{H}_2(\text{NO}_2)_3\text{OH}$), was discovered by J. A. Glauber in the seventeenth century. He obtained it by treating wood with nitric acid. In 1771 Woulfe accidentally obtained picric acid by the action of nitric acid upon indigo. Picric acid has long been produced by the nitration of phenol, a derivative of coal tar. It is a yellow solid, is fairly soluble in hot water, and has an intensely bitter taste. Sprengel (1871) discovered that this acid may be detonated by fulminate of mercury. It is a yellow dye for silk and wool. Picric acid is 1:2:4:6-trinitrophenol:



The alkali salts of picric acid (*picrates*), such as $\text{C}_6\text{H}_2(\text{NO}_2)_3.\text{OK}$, explode violently on percussion or when heated.

William Perkin, a young English chemist, treated (1856) aniline with potassium dichromate, hoping to oxidize it to quinine. Instead of producing quinine, he synthesized the first of the basic coal tar colors, and named it "mauve." This complex dye was the beginning of the coal tar dye industry. Since the discovery of mauve innumerable dyes have been synthesized from coal tar compounds. Indeed, nearly all the dyes employed at present are

artificial organic dyestuffs, such as mauve, magenta, alizarin, and indigo.

Indigo ($C_{16}H_{10}N_2O_2$) is one of the oldest and fastest of dyes. Certain tropical plants contain a glucoside known as *indican*, which yields **indigo blue**, or **indigotin**. When the leaves and stems of the indigo plant are steeped in lukewarm water and allowed to ferment, a yellow liquid is obtained which contains *indigo white* ($C_{16}H_{12}N_2O_2$). When the solution of indigo white is violently agitated in the presence of air, the indigo white is transformed into insoluble indigo blue. As late as 1897 India devoted about a million acres to the cultivation of the indigo plant, but indigo is now produced on a large scale from naphthalene.

Madder is an Old World perennial plant, the roots of which have furnished red coloring matter for centuries. The active coloring principle extracted from the roots is **alizarin** ($C_{14}H_8O_4$), known as "Turkey red." Alizarin is now produced more economically from anthracene ($C_{14}H_{10}$), so the madder fields of France have been put to other uses.

With an aluminium mordant, alizarin yields Turkey red, one of the finest of red dyes.

In order that a colored substance may fulfill the requirements of a dye, it must be capable of fixing itself, or of being fixed, in the material to be dyed, so firmly that the color is fast when the fabric is rubbed, or when washed with water.

Dyestuffs may be divided broadly into the two classes — *substantive* and *adjective*.

Substantive dyestuffs produce a finely developed color on the textile material without the aid of any other combining substance or chemical. In other words, a direct color is produced. Thus, picric acid (yellow) is fast on silk and wool, and congo-red is fast on both wool and cotton. Indigo is also a direct dye. *The greater number of organic dyes are direct dyes on wool and silk.* As a rule, it appears that direct dyes are either basic or acidic in character. Silk and wool appear to contain both basic and acidic components.

Adjective dyestuffs require an intermediate combining substance or chemical, called a **mordant** (Lat. *mordere*, to bite), to fix and fully develop the color: *e.g.*, aluminium hydroxide may be employed to fix alizarin to cotton textiles, giving Turkey red. Cotton is rather inactive chemically and has less tendency than have silk and wool to form direct colors.

Mordants are generally of a colloidal nature and have therefore

great adsorptive power. Aluminium hydroxide, for instance, may be employed to precipitate many dyestuffs from solution, forming insoluble colored materials known as lakes. When a material is dyed, the coloring matter appears to be adsorbed by the mordant forming an insoluble **lake** within the fibers.

The formation of lakes may be shown by the following *experiment*:

Place in one large beaker a very dilute solution of aluminium sulfate and in a second jar, very dilute ferric chloride; then add a few drops of a solution of alizarin to each, followed by a small quantity of sodium hydroxide solution, in order to precipitate the hydroxide of the metal. The dye forms a lake in each case. With aluminium hydroxide, the color should be red, while the other should be violet or dark purple.

It may be of interest to add that the minute fibers of cotton and wool are cylindrical or flattened tubes, while silk fibers are solid. The walls of these fibers, like parchment paper and special membranes, allow water and substances in true solution to pass through, but do not allow colloids to pass. Since picric acid can be washed out of cotton but is fast with silk and wool, it may be inferred in the latter case that it forms some sort of chemical combination with the constituents of silk and wool. The true nature of the fast or insoluble compounds or products formed in dyeing is in many cases very obscure; but in some cases it no doubt comes under the head of adsorption.

FLAME

738. Definition of Flame. — Flame, in the popular sense, is a gas burning in air. Thus, when coal gas burns, heat and light are produced. The production of flame is, however, not confined to a gas burning in air; it is the phenomenon observed when any two gases combine, *i.e.*, undergo combustion, accompanied by the evolution of heat and light: *e.g.*, hydrogen burns in chlorine to form hydrogen chloride.

When such fuels as oils, fats, wood, and coal burn, the volatile matter forms gases or vapors, which burn, producing flame. Charcoal and coke burn with the production of heat and light, but very little flame, owing to the fact that the volatile matter has been expelled from the fuel. Likewise, iron burns brilliantly in oxygen, but the combustion of the metal does not produce a flame.

739. The Reversibility of Flame. — *Combustion is a relative phenomenon.* We ordinarily say that air or oxygen is "incombustible," for we think of oxygen as a supporter of combustion.

It can be shown very readily, however, that air (oxygen) will burn in an atmosphere of coal gas or of hydrogen. In this case, coal gas or hydrogen is the supporter of combustion — just the reverse of combustion in the ordinary sense.

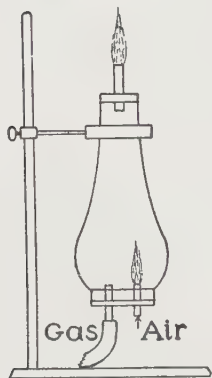


FIG. 203.

This may be shown by the following *experiment* (Fig. 203):

Close with a cork the lower end of a long lamp chimney. Through one opening in the cork pass a tube for the introduction of illuminating gas or hydrogen, and through the other opening insert a short straight, brass or glass tube. The upper end of the chimney also is closed with a cork bearing another straight tube. Turn on the gas at medium pressure, and after the air is displaced, ignite the gas as it issues from the small tube at the bottom of the chimney. When the stopper is removed from the tube, the upward draft causes the flame of the burning gas to recede up the tube, and we have a flame produced

by air (oxygen) burning in an atmosphere of coal gas or hydrogen. Now light the gas as it escapes from the tube at the top of the chimney. (Explain.)

Oxygen may be burned by heating potassium chlorate in a deflagrating spoon and then plunging it into a lamp chimney through which coal gas is being passed. The spoon is inserted through a hole in an asbestos board resting on top of the chimney. The escaping gas is ignited before introducing the hot potassium chlorate.

The products of combustion are identical, whether we burn coal gas in oxygen, or oxygen in coal gas; for combustion is a mutual act. In other words, a supporter of combustion may be made to undergo combustion, and a combustible gas (in the ordinary sense) may be made the supporter of combustion.

740. Luminosity of Flame. — It is a matter of common observation that some flames are very luminous and others are practically non-luminous. Thus, ethylene and acetylene burn with luminous flames, while hydrogen, carbon monoxide, and methane (natural gas) burn, producing but little light. How may this fact be explained? A general explanation to cover all cases of luminosity cannot be given. It may be stated in general, however, that the luminosity of flame is dependent upon, or influenced by, the following factors:

- (1) *The glowing of solid matter, such as carbon (Davy, 1818).*
- (2) *The luminosity is increased by increasing the pressure of the burning gases.*
- (3) *The luminosity is increased by raising the temperature.*

(1) The luminosity of flames of burning hydrocarbons is due largely to solid particles of carbon heated to incandescence. A hydrocarbon (*e.g.*, ethylene, C_2H_4) dissociates when heated:



This can be shown by holding a porcelain dish in the flame of burning ethylene or acetylene. A deposit of soot (carbon) is obtained upon the dish (compare the combustion of H_2S , 326).

Ethylene, acetylene, and benzene burn, yielding much more light than does methane, for they are much richer in carbon. Hydrogen and water gas ($CO + H_2$) produce much heat, but little light, when burned. The luminosity of such gases may be increased by mixing them with hydrocarbons rich in carbon. A gas thus treated is known as an "enriched (carbureted) gas." Thus, when hydrogen is bubbled through liquid benzene and then burned, it produces a very luminous flame, for the vapor of benzene, C_6H_6 , is carried over.

When the oxyhydrogen flame is directed upon a stick of calcium oxide (quicklime), an intense light (Drummond) is produced. To increase the luminosity of the flames of natural gas and water gas, the gases may be burned in contact with the **Welsbach mantle**, which consists of 99 per cent of thorium dioxide (ThO_2) and 1 per cent of cerium dioxide (CeO_2). The oxides are heated to incandescence and glow brilliantly.

(2) That the density of the burning gases has an influence upon the luminosity of flame, was observed by Frankland about 1868. He noticed that a flame of a candle burning on the top of Mont Blanc emitted much less light than when burning in the valley below. Frankland conducted various experiments, and arrived at the conclusion that dense gases and vapors become "luminous at a much lower temperature than the same gases in a more rarefied condition."

(3) That the luminosity of a flame may be increased by heating the gas before combustion, may be shown by passing coal gas through an elongated Bunsen burner lying in the horizontal position in an ordinary combustion furnace. When the air-holes of the burner are open, the cold gas burns with a blue flame; but when the burner is heated, the luminosity of the flame increases with rise in temperature.

The luminosity of flame, on the other hand, may be decreased by admitting cold air, or by mixing the gas with an indifferent gas, such as carbon dioxide or nitrogen.

741. **The Structure of Flame.** — The hydrogen flame is very simple. When the gas is allowed to escape through a circular jet and ignited, it burns with a non-luminous flame, which is a cone

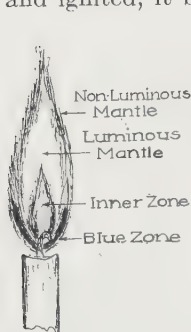


FIG. 204.

with a sheath or mantle of burning gas. In general, a gas issuing from a circular jet burns, producing a flame which assumes the form of a cone. The interior of the flame where air is absent is unburnt gas.

When a candle burns, the hydrocarbons are drawn up through the wick by capillary action, and vaporized. The *inner zone* (Fig. 204) consists of unburnt gas. Above and surrounding this zone there is a *luminous mantle* (partial combustion), and outside of this a *non-luminous mantle* (complete combustion). At the base of the flame there is a *blue zone*.

Figure 205 shows in detail the various parts of the flame of the **Bunsen burner** (after Fresenius).

(1) *aaa'a'* is the dark cone. It is made up of cold gas mixed with about 62 per cent of air.

(2) *a'cab* is the mantle formed by the burning mixture of gas and air.

(3) *aba* is the luminous tip of the dark cone, which appears only when the air-holes are somewhat closed. This tip is very useful for reductions. These are the principal parts of the flame.

According to Bunsen, there are no less than six parts of the flame, which he names as follows:

1. *The base A.* Here the temperature is relatively low.
2. *The fusing-zone B.* This is somewhat more than one-third from the bottom of the flame and equidistant from the inside and the outside of the mantle, which is broadest at this point. This is the hottest part of the flame; the temperature may reach 1,500° C. or more.
3. *The lower oxidizing flame C.* It lies in the outer border of the fusing-zone. This flame is well adapted to the oxidation of substances in various fluxes.
4. *The upper oxidizing zone at E.* Its action is strongest when

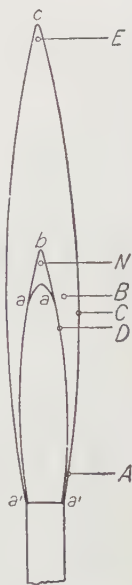


FIG. 205.

the air-holes are open. This flame is used for the process of oxidation when the very highest temperature is not required.

5. *The lower reducing-zone at D.* This is located in the inner border of the fusing-zone next to the dark cone. In this zone the reducing gases are mixed with oxygen, and we do not get the full reducing effect. It is especially good for the reduction on the charcoal stick.

6. *The upper reducing flame at N.* This is in the luminous tip of the dark inner cone. This part of the flame must not be allowed to get large enough to blacken a test-tube filled with water and held in it. It is very useful in the reduction of metals collected in the form of incrustations.

742. **Burners.** — The Bunsen burner allows air to enter at the side-holes and mix with the gas before combustion occurs, which results in a non-luminous flame; for the liberation of carbon is prevented owing to the fact that air cools the middle zone of the flame, thus preventing the dissociation of the ethylene. Nitrogen or carbon dioxide has the same effect.

It may be shown that the inner cone of the Bunsen burner contains unburnt gas by inserting in it one end of a glass tube and igniting the gas as it issues from the other end. By lowering a wire-gauze in the flame a red-hot ring is produced, showing that the interior of the flame is at a low temperature. Likewise, paper is charred in the form of a ring when pressed down for a moment upon the flame of the burner.

The flame of the Bunsen burner sometimes "strikes back." This phenomenon can be produced by gradually turning off the gas until a point is reached where there is too much air in proportion to the gas. The result is that an explosive flame travels down the tube, *i.e.*, the flame "strikes back." In order that the gas may burn quietly, it must be mixed with the proper proportion of air.

When the air-holes of the Bunsen burner are closed, the flame is luminous ("smoky"), owing to incomplete combustion.

The burners on a gas range are modified Bunsen burners (Fig. 206), for gas mixes with air before it is burned.

The **Méker burner** and the **Fisher burner** produce a very high temperature. The gas is supplied with a large quantity of air, and a grid on top of the burner prevents the flame from "striking back." There is practically a "solid cone" of burning gas.

The temperatures of the Fisher and Bunsen flames are shown in Fig. 207.

The **blast-lamp** also produces a higher temperature than the Bunsen burner, for a bellows is employed to force a larger proportion of air into the gas; also, the gases move more rapidly than in an ordinary flame, so the heat reaches the body faster.

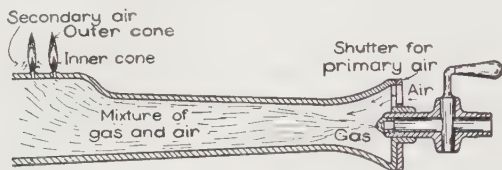


FIG. 206.

743. The Davy Lamp. — When a wire gauze is held a few inches above a Bunsen burner, it is possible to burn the gas above the gauze without the gas below igniting. This is due to the fact that the iron gauze is such a good conductor of heat that the gas below the gauze is not raised to its kindling temperature.

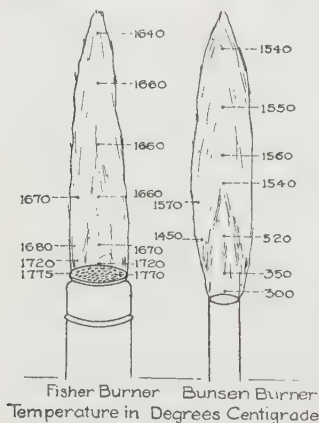


FIG. 207.

Sir Humphry Davy (1815) made use of this principle in the construction of a *miner's lamp*. A wire gauze is substituted for the chimney of a lantern. When a safety-lamp is carried into a mine containing fire-damp, the explosion is confined to the interior of the lamp, for the gauze conducts away the heat so rapidly that the gas outside does not reach the temperature of ignition. In a similar way, by placing a small

coil of cold copper wire over a candle flame so much heat may be conducted away that the flame is extinguished.

744. Detection and Analysis of Carbon Compounds. — *It is characteristic of organic compounds when suddenly brought to a high temperature, to char or turn black, for carbon is liberated.* Carbonization is usually carried out in a small glass tube sealed at one end, and blackening is ordinarily accompanied by a burnt odor, as so well exemplified by burnt sugar.

When aromatic compounds, hydrocarbons, unsaturated fatty

compounds, and fatty compounds containing more than four carbon atoms are burned on a short roll of fine copper gauze, soot is usually produced.

When organic salts of alkali and of alkaline earth metals are ignited, they yield carbonates. For example, when sodium acetate is ignited in a crucible, sodium carbonate is formed; the product effervesces (CO_2) when a drop or two of hydrochloric acid is added.

In analysis, carbon compounds are first oxidized. *Carbon* forms carbon dioxide, which may be detected by limewater; *hydrogen* is converted into water; *sulfur* is oxidized to sulfuric acid, and *phosphorus* to phosphoric acid; *nitrogen* is set free; *halogens* yield the corresponding halides when the organic compounds are oxidized in the presence of silver nitrate.

In testing for carbon, hydrogen, and nitrogen, cupric oxide is generally employed as an oxidizing agent. The carbon compound is mixed with CuO and heated in a hard-glass tube. Sulfur, phosphorus, and halogen compounds may be oxidized with concentrated nitric acid. Furthermore, nitrogen in many organic substances, *e.g.*, gelatine, yields ammonia when heated with soda-lime; halogen compounds form calcium halides. Sulfur can be detected in many cases by heating the carbon compound with a small piece of sodium in a narrow ignition tube. Sodium sulfide is formed, which blackens a wet silver coin.

EXERCISES

1. What is meant by organic chemistry? Explain the significance of the synthesis of urea by Wöhler in 1828.

2. Outline the chief sources of carbon compounds.

3. State the basis for the classification of organic compounds.

4. State the chief sources of hydrocarbons. Explain what is meant by an homologous series of hydrocarbons, and illustrate by writing the names and formulae of three members of three different series.

5. Account for the occurrence of methane in nature. Methane is one of the paraffins. Explain. Why are methane and similar substances called saturated compounds?

6. Compare the efficiency of hydrogen and of methane in lifting a balloon in air.

7. (a) Define or explain, also illustrate, the following: (1) substitution; (2) destructive distillation; (3) fractional distillation; (4) "cracked" hydrocarbons; (5) isomerides.

(b) Write the formulae and names of the isomerides of pentane.

8. Give an outline of the occurrence and the composition of petroleum, and state the chief products obtained from it.

9. Outline what has been accomplished in the production of synthetic fuels.

10. Describe the preparation and the properties of ethylene and acetylene. What products are always formed when hydrocarbons are burned? Illustrate by writing chemical equations to show the combustion of ethylene and acetylene. Why is it dangerous to compress acetylene in supply cylinders?

11. Explain how you would distinguish a saturated hydrocarbon from an unsaturated one. Show that ethylene and acetylene are unsaturated compounds.

12. When a mol (26 g.) of acetylene is burned in oxygen, 310,000 are produced. Compare the heat of combustion of acetylene with the combined heat formed by burning separately 24 g. of pure carbon and 2 g. of hydrogen. Explain.

13. Explain the significance of the statement that, "nearly all carbon compounds are endothermic." Are starch and cellulose endothermic? Are they explosive?

14. Outline the preparation of coal gas, and point out the chief by-products obtained; also wood gas.

15. Give the names and formulae of some of the chief substances obtained from coal.

16. What are aromatic compounds? Write the structural formulae for benzene, toluene, naphthalene, carbolic acid, and aniline.

17. When toluene is nitrated, what very important substance is formed? By analogy, show that mononitrobenzene can be formed by nitrating benzene.

18. Define and illustrate what is meant by flame. Explain fully what is meant by the reversibility of flame. Show that oxygen is really a combustible gas.

19. Explain why some flames are luminous, while others are practically non-luminous. How would you prove that a hydrocarbon dissociates before burning?

20. Cite experimental evidence to prove the structure of flame.

21. Upon what principle did Davy construct a lamp for miners? Explain why the flame of a Bunsen burner often "strikes back." Why does a blast-lamp produce a higher temperature than a Bunsen burner?

22. How would you show experimentally that methane contains the same amount of hydrogen but only half as much carbon as ethylene?

23. How would you distinguish between an organic and an inorganic compound? Illustrate. Do all carbon compounds char when heated, and do any non-carbon compounds turn black when ignited? Give examples to illustrate your answer.

24. How could you prove that the following elements are constituents of an ordinary egg: carbon, hydrogen, nitrogen, sulfur, and phosphorus?

25. Analysis of a compound containing carbon, hydrogen, oxygen, and nitrogen yielded the following numbers: 0.2425 g. of substance, when oxidized, gave 0.55 g. of CO_2 and 0.1575 g. of H_2O . Also, 0.2425 g. of substance yielded 30.6 cc. of nitrogen, measured over water at 20°C . and 765 mm. barometric pressure. Find the empirical formula of the compound.

(*Note.* — First find the percentages of carbon, hydrogen, and nitrogen; the oxygen may then be found by difference.)

26. State some of the differences between aliphatic and aromatic compounds.

27. What are substantive and adjective dyes? What is a lake?

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CHAPTER XLI

SOME IMPORTANT CLASSES OF CARBON COMPOUNDS

CARBOHYDRATES

745. Definition and Classification. — The term “carbohydrate,” as commonly used, refers to certain compounds containing carbon, hydrogen, and oxygen, which are among the chief products of vegetable life, and in which the ratio of hydrogen to oxygen is usually the same as in water $C_n(H_2O)_m$. These compounds might be represented, then, as being composed of carbon and water; hence the name carbohydrate (or hydrate of carbon): *e.g.*, the formula of glucose, $C_6H_{12}O_6$, might be written $6C.6H_2O$. This does not mean that a carbohydrate contains water, but only the elements of water.

The carbohydrate group is closely related to life, for it contains substances used as food and from which important fabrics, such as clothing and paper, may be manufactured. *The carbohydrates are divided into the following classes:*

- (I) **The Sugars** (cane sugar, glucose, fructose, etc.).
- (II) **The Starches** (the most abundant of all foods).
- (III) **The Celluloses** (the principal substances of cell membranes and plant tissues).

The common sugars may be divided thus:

- (1) *The Monosaccharoses*¹ having the formula $C_6H_{12}O_6$:
Glucose, dextrose, or grape sugar,
Fructose, or fruit sugar.
- (2) *The Disaccharoses*, $C_{12}H_{22}O_{11}$:
Sucrose, or cane sugar,
Lactose, or milk sugar (4 to 5 per cent in cow's milk),
Maltose (formed by action of malt or diastase on starch).

The starches and celluloses have the general formula $(C_6H_{10}O_5)_x$, and are called *polysaccharoses*. Under this term we find starch, cellulose, inulin, glycogen, dextrin, and the gums. The molecular

¹ Some writers use the terms *monosaccharides*, *disaccharides*, etc.

weights of the starches and celluloses are unknown, but to simplify the writing of equations their composition may be represented by the empirical formula $C_6H_{10}O_5$.

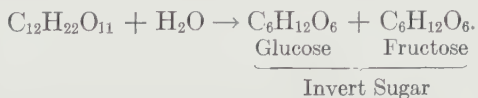
THE SUGARS

746. Cane Sugar or Sucrose, $C_{12}H_{22}O_{11}$. — Sucrose (ordinary sugar) is found chiefly in the sugar cane and the sugar beet; it also occurs in the sugar maple and in honey. The sugar cane was originally grown in India and Arabia and was introduced into Southern Europe by the Arabs. The sugar cane contains from 16 to 18 per cent of sugar. Sugar was discovered in beet root by the German chemist Marggraf in 1747. At that time there was about 6 per cent of sugar in the beet, but by cultivation the percentage has been increased to 13 to 16.

Sugar is obtained from the sugar cane by crushing the stalks between rollers; but the beet roots are cut into slices, and the sugar extracted by a diffusion process. After appropriate preliminary treatment, the sugar solution is evaporated under reduced pressure at about 65° to prevent decomposition of sugar. The syrup obtained, upon cooling, yields crystals of brown sugar, which can be refined by dissolving in water, filtering through boneblack, and evaporating in vacuum pans until sugar crystallizes out. In 1913 the cane and the beet each supplied about 9,000,000 tons of sugar. In 1924, the world's production of sugar was over 23,000,000 tons, 35.4 per cent of which was from the beet.

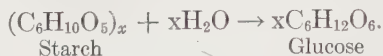
Sucrose is very soluble in water and melts at 160° . When sugar is heated to about 200° to 210° , it loses water, and is gradually converted into a brown mass known as *caramel*. This substance is used for coloring liquors and soups.

When sucrose is boiled with water containing a little acid, the hydrogen-ion of the acid acts as a catalyst, and the sugar is hydrolyzed to glucose and fructose ("invert sugar"):



The mixture of the isomers glucose and fructose is a sticky mass, which is used in the manufacture of preserves, confectionery, etc. Each sugar interferes with the crystallization of the other, because of the lowering of the freezing point (177). Invert sugar is therefore used in making soft candy, or candy that is to be "pulled."

747. **Glucose, $C_6H_{12}O_6$.** — Glucose (*dextrose* or *grape sugar*) occurs in many fruits, particularly the grape; hence its name. It is often associated with fructose in many sweet fruits and in honey. Glucose is manufactured on a large scale by boiling starch with a dilute acid, which plays the rôle of a catalyst:



Upon neutralizing the acid, glucose may be obtained as a crystalline mass by evaporating the solution. Corn syrup contains glucose (40 to 50 per cent), dextrin, and water.

Pure glucose is almost colorless, and is quite soluble in water. It is not as sweet as sucrose. Glucose is dextrorotatory, *i.e.*, its solution rotates the plane of polarization to the right. Glucose is a good reducing agent; it reduces Fehling's solution,¹ forming a red precipitate of cuprous oxide (Cu_2O).

When glucose is persistently present in urine, it is a distinguishing mark of the disease known as *diabetes mellitus*. In case of this disease there is a deficiency of insulin supplied by the pancreas, and the carbohydrates are not thoroughly burned. Just how the insulin acts is not known. When metabolism of sugar fails, fats and proteins cannot be properly digested or utilized. In case of diabetes, insulin is now administered subcutaneously. Fehling's solution is utilized to determine the amount of the sugar in urine, which sometimes amounts to 8 to 10 per cent.

Glucose solution reduces copper sulfate to a yellow precipitate of cuprous oxide (Cu_2O), which rapidly turns red. Sucrose does not reduce Fehling's solution.

Glucose ferments with yeast, in dilute aqueous solution, yielding principally alcohol and carbon dioxide:

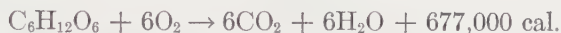


Glucose is used extensively in the manufacture of confectionery, jams, jellies, etc.

¹ **Fehling's solution** is composed of two solutions — No. 1 and No. 2. No. 1 is made by dissolving 69.3 g. of pure $CuSO_4 \cdot 5H_2O$ in water and diluting to 1,000 cc. No. 2 is prepared by dissolving 350 g. of Rochelle salt and 100 g. of NaOH in water and diluting to 1,000 cc. These solutions are kept in separate bottles, and equal volumes are measured out and mixed for immediate use. In the analysis of a solution containing glucose, a measured volume of Fehling's solution is boiled in a flask, and the sugar solution is then added gradually from a burette until the copper is precipitated as Cu_2O .

The sugars are very important as food. When sugar is assimilated, it is oxidized to CO_2 and H_2O with the production of energy. Sucrose is split mainly by the enzyme sucrase of the intestinal juice, glucose and fructose being formed.

The heat of combustion of glucose is shown by the following equation:



This is somewhat analogous to the combustion of fuel in an engine, and is the converse of the formation of carbohydrates in the leaves of green plants (764).

STARCH AND CELLULOSE

748. **Starch** ($\text{C}_6\text{H}_{10}\text{O}_5$)_x. — Starch is the most abundant of all foods. It occurs in various plants, being stored largely in the seeds of grains and the tubers of the potato. We have seen how starch is built up by plants from carbon dioxide and water, under the influence of solar energy (436). The following are the average percentages of starch present in the potato, cereals, maize, and rice:

Potato.....	15-20 per cent
Wheat, and other cereals.....	60-65 "
Maize.....	65 "
Rice.....	75-80 "

Starch consists of minute colorless granules, which differ somewhat in appearance according to its source. Thus, the granules may be round, elliptical, or angular, and they consist of concentric layers or rings arranged round a nucleus.

In the United States starch is obtained chiefly from maize, whilst potatoes are the chief source in Germany, and rice in England. The process of manufacture is largely mechanical. The softened or crushed material is washed so as to pass the granules of starch through a fine wire or silk sieve, leaving the gluten behind (3).

Starch is insoluble in cold water, but when it is treated with hot water the granules burst and the substance goes into colloidal solution, *i.e.*, the very finely divided particles are suspended in water. Colloidal solutions of starch are used in the laundry. Colloidal starch turns blue in the presence of iodine (delicate test). When, therefore, iodine is dissolved in a solution of potassium iodide and some of the brown solution placed on a plant, *e.g.*, the leaf, the granules of starch turn blue, while the other parts are not affected.

Starchy foods are made more digestible by cooking. During the

process of digestion, starch is first converted into the simpler sugars by the agency of the digestive fluids.

Starch is the starting point in the manufacture of large quantities of alcohol and alcoholic beverages.

Dextrin ($C_6H_{10}O_5$)_n may be obtained by gently heating starch (210°), or by moistening starch with a mixture of dilute nitric and hydrochloric acids, and heating to 100° to 125°. It is sold under the name of British gum, and when treated with water it forms a clear mucilage.

749. Cellulose ($C_6H_{10}O_5$)_y. — Cellulose is very abundant, for it constitutes the framework of all vegetable tissues and forms the walls of cells, which explains the origin of its name. When linen, cotton, hemp, and flax have been freed from inorganic matter by treatment with appropriate chemicals, they are almost pure cellulose. Swedish filter paper is essentially pure cellulose.

Cellulose is insoluble in all the ordinary solvents, but dissolves in an ammoniacal solution of cupric oxide and in a hot solution of zinc chloride. The cellulose is probably taken into colloidal suspension. When the former solution is acidified, the cellulose is recovered. From the solution in zinc chloride, cellulose may be precipitated in the form of a thread by forcing the solution through an orifice into alcohol. Carbon filaments for incandescent bulbs may be prepared by carbonization of these threads.

Cotton (cellulose) is not soluble in a boiling solution of sodium hydroxide, whilst wool is soluble. When small pieces of fabric are boiled with caustic soda solution, a residue of cellulose is left in case the material is partly cotton.

It is of interest to note that concentrated sulfuric acid gradually dissolves cellulose, and when the solution is diluted with water and boiled, glucose is ultimately produced. It is therefore possible to produce sugar (glucose) and ethyl alcohol from wood, paper, or rags.

The colloidal nature of cellulose and of its derivatives accounts for their innumerable uses. Cellulose derivatives are characterized by high plasticity. Another valuable property of cellulose is its chemical indifference to the atmospheric agency. Besides paper, explosives, collodion, and rayon (artificial silk), cellulose provides us with artificial ivory. Numerous articles, such as toilet articles, are manufactured from "ivory pyralin."

Nitrocellulose is manufactured by treating cellulose with a mixture of nitric and sulfuric acids (389). It is extensively used in the manufacture of collodion, celluloid, explosives, etc.

750. **Paper.** — As previously stated, paper is produced principally from wood fiber. The production of paper is partly a chemical process, being more complicated when wood, straw, and grass are used as a source of the fiber than when rags are used. The raw materials are first "cooked" with appropriate chemicals in order to secure the fiber. With wood the sulfite process (337) is most widely employed. The chemical dissolves the non-cellulose components, such as lignin, leaving the more resistant cellulose. The fiber is thoroughly washed with water and the material screened. The fiber is then bleached by means of a hypochlorite (308). It is next beaten in tubs, dyed if a colored product is wanted, and then sized. **Sizing** prevents the spreading of ink, which is an essential quality of writing paper but not for newspaper. Sizing is accomplished by means of such substances as rosin and alum, which are passed into the beater with the pulp. Paper may be "**loaded**" by adding pulverized gypsum and certain other white substances; and it may be given a smooth surface by treatment with casein, a product from milk.

Paper is manufactured by means of machines, which are from 100 to 240 inches wide. These produce paper continuously. A large paper machine has a capacity of about 150 tons in 24 hours, and can produce paper at the rate of more than 1,000 feet per minute.

751. **Rayon.** — The production of **rayon**, or **artificial silk**, has made very rapid progress in recent years. This is also a chemical process, or is controlled by chemistry.

Artificial silk is composed of filaments of cellulose. The first successful fiber was produced by Chardonnet in 1884. In this process collodion (389), is forced through very fine glass nozzles.

Three processes are employed in the manufacture of rayon, all of which are based upon forcing a solution of cellulose through a minute orifice, the stream of solution being precipitated in the form of a fiber. The chemist in this case has learned a lesson from the silkworm, which ejects through two very fine spinnerets a semi-liquid material which hardens quickly into fiber.

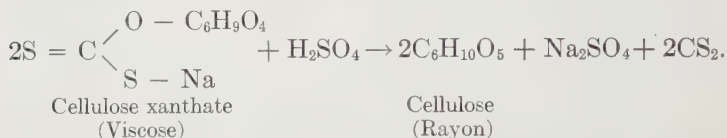
The processes employed differ by the method of preparing the solution of cellulose, and are as follows:

- (1) **The Cellulose Nitrate Process;**
- (2) **The Cuprammonium Process;**
- (3) **The Viscose Process.**

At the present time by far the greatest part of rayon is produced by the viscose process. When "mercerized" cellulose (cellulose

treated with sodium hydroxide solution), such as that obtained from spruce, is treated with carbon disulfide, *xanthate of cellulose* is formed, the alkali solution of which is called "viscose." This product possesses high viscosity, and when it is forced through very fine orifices (about 0.004 inch) into a strongly acidulated bath, coagulation occurs at once, the cellulose being precipitated in the form of a flat ribbon-like thread, which is desired for the production of soft, pliable silk.

According to M. G. Luft, the spinning reaction of viscose can be represented in the final stage by the following equation:



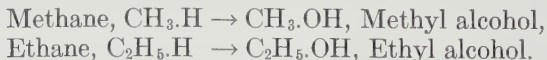
After spinning, the fiber is washed, desulfurized, and bleached (Fig. 208). Artificial silk may be dyed most beautifully.

The raw material used in the viscose process is bleached cellulose from spruce, bleached cotton linters, or a mixture of the two. In 1925 about 80 per cent of the world's production of rayon was by the viscose process.

Artificial silk may be identified by its physical and chemical properties. Real silk, the product of the silkworm, is a nitrogenous compound, and in its chemical behavior is very similar to wool.

ALCOHOLS

752. Definition of the Term, Alcohol. — An alcohol is a hydroxide of an organic radical (726). Those containing one hydroxyl group have the general formula, $\text{C}_n\text{H}_{2n+1}\text{OH}$ or ROH . We may regard them as being derived from the paraffins by the substitution of the hydroxyl group for one atom of hydrogen:



These alcohols are the first members in an homologous series (723).

Glycerine or **glycerol**, $\text{C}_3\text{H}_5(\text{OH})_3$, is an alcohol belonging to another series; it is called a trihydric alcohol.

Alcohols are somewhat analogous to bases, but they do not ionize in water to furnish the hydroxide-ion.

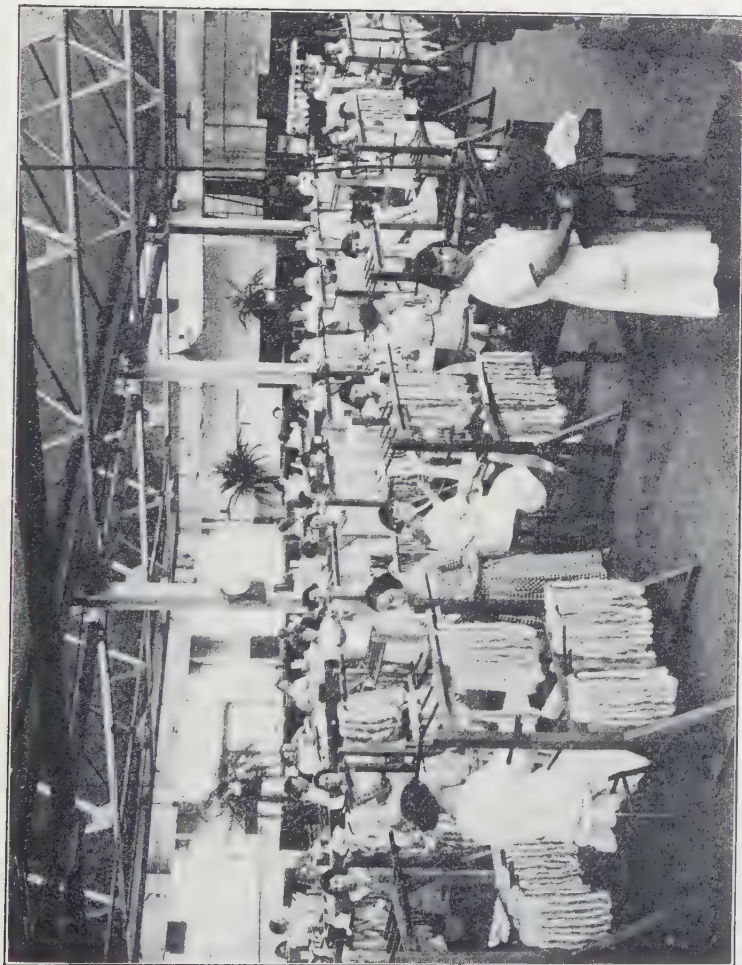
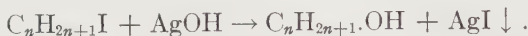


FIG. 208. THE MANUFACTURE OF RAYON.

Rayon, or the so-called artificial silk, is spun from material derived from wood or cotton.

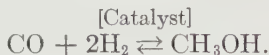
Courtesy of Industrial Fiber Co.

Alcohols of the series $C_nH_{2n+1}.OH$ can be prepared by the action of moist silver oxide upon alkyl halides:



753. Methanol, Methyl Alcohol, or Wood Spirit, CH_3OH . — This compound occurs in nature in combination in certain essential oils: *e.g.*, oil of wintergreen contains methyl salicylate, which is the methyl ester of salicylic acid, $C_6H_4 \begin{smallmatrix} \swarrow COOH \\ \searrow OH \end{smallmatrix}$

Methyl alcohol may be obtained by the destructive distillation of wood. The pyroligneous liquor (or acid) obtained contains a low percentage of the alcohol, as well as acetic acid, acetone, etc. From the liquid, methyl alcohol is prepared; hence it is known as "wood spirit" or "wood alcohol." Until recently this was the sole commercial source of methanol, but now it is produced by passing water gas ($CO + H_2$) under high pressure over a catalyst (*e.g.*, $ZnO + Cr_2O_3$):



Methanol is obtained as a by-product of the Haber process (or its modification) for synthetic ammonia (376). The alcohol is of high grade and the process for its production so economical that the old wood alcohol industry is threatened.

Pure methyl alcohol is a colorless liquid with a specific gravity of 0.796 at 20° ; it boils at 66° , possesses a wine-like odor and a burning taste, and mixes with water in all proportions. The alcohol burns with a pale, non-luminous flame, with the production of much heat:



It is quite poisonous when taken in concentrated form, and has the property of affecting the optic nerve, producing blindness. The late Professor Duncan stated that, "out of 10 men who drink 4 ounces of pure methyl alcohol in any form whatever, 4 will probably die, 2 of them becoming blind before death. The remaining 6 may recover, but of these 2 will probably be permanently blind."

Methyl alcohol is a good solvent for shellacs and resins, and is used extensively in the manufacture of varnishes, organic dyes, methylated spirit, formaldehyde, etc.

The crude "wood spirit" of commerce contains acetone and other impurities.

754. Ethyl Alcohol, C_2H_5OH ; Fermentation. -- Ethyl alcohol is also called *grain alcohol* and *spirit of wine*; it has been known since ancient times, for it is contained in all fermented liquors. Like methyl alcohol, it occurs in plants in combination.

Alcohol can be prepared by the fermentation of sugars and molasses. By placing an aqueous solution of glucose (5 to 10 per cent) in a flask and adding a few small pieces of brewer's yeast and setting the flask in a warm place (20° to 30°), fermentation soon sets in, alcohol and carbon dioxide being produced:



By fitting the flask with a cork and a delivery tube the formation of carbon dioxide can be proved by passing the evolved gas through limewater. When the fermentation is at an end, the alcohol may be concentrated by fractional distillation. If lime be added to the distillate, water is taken up, and by distilling a second time a more concentrated product is obtained.

Large quantities of commercial alcohol are manufactured by the fermentation of molasses, a by-product of sugar mills. In 1924 the United States produced nearly 120,000,000 gallons from this source alone.

How is **fermentation** (Lat. *fervere*, to boil) brought about? It has been established by experiment that fermentation is induced by certain enzymes which occur in plants. Enzymes are catalysts produced by living organisms; they are found in both plants and animals, and the mere presence of these complex, mysterious substances is sufficient to induce many chemical changes. Enzymes play a great rôle in fermentation, digestion, etc. Yeast consists of microscopic cells belonging to a low order of plants, in which two important **enzymes** — *zymase* and *sucrase* (invertase) — are secreted. When yeast is added to a solution of glucose, zymase acts as a catalyst in converting the sugar into alcohol and carbon dioxide. A solution of cane sugar ferments more slowly, for the enzyme sucrase first induces sucrose to change, by the addition of water, into invert sugar (746). The glucose and fructose are then fermented by zymase.

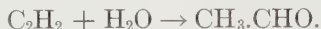
Alcohol is manufactured on a large scale from grain, potatoes, and other starch-containing materials. The raw material is reduced to a pulp or paste, a little *malt* (from barley or other grain) added, and the starch fermented to *maltose* (a sugar) and dextrin.

The enzyme *diastase*, present in malt, induces the change:



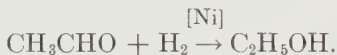
Yeast is now added, and the solution kept until the alcoholic fermentation is at an end. Maltase (present in yeast) hydrolyzes the maltose to glucose, and zymase ferments it. The weak solution of alcohol obtained by fermentation is subjected to fractional distillation.

Ethyl alcohol also can be produced by synthesis. Thus, when acetylene, C_2H_2 , is led into a hot concentrated solution of sulfuric or phosphoric acid in which a salt of mercury is dissolved, acetic aldehyde, CH_3CHO (759), is formed:

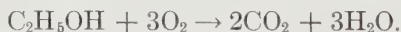


The acid serves as catalyst and the mercury salt is a promoter of the action.

Ethyl alcohol may be formed by passing a mixture of acetaldehyde and hydrogen over a catalyst, such as nickel:



Pure ethyl alcohol is a colorless liquid having a specific gravity of 0.806 at 0° and of 0.793 at 15° . Its boiling point is 78.3° , it freezes at -112° , and mixes with water in all proportions. It burns, forming carbon dioxide and water:



Iodoform, CHI_3 , a yellow, crystalline compound with a characteristic odor, is formed when iodine and soda (or potash) interact with ethyl alcohol. Methyl alcohol does not form iodoform, and its density and boiling point differ from those of ethyl alcohol.

The Federal Government imposes a heavy tax on ordinary 95 per cent alcohol. For commercial purposes, **denatured alcohol** is employed; it is prepared by adding substances which render it unfit for use as a beverage. Wood alcohol, pyridine, and benzine are common denaturants.

Alcohol is used extensively as a solvent (varnishes, etc.), as a fuel, and for the production of ethylene (728). On account of its efficiency and its colorless flame, alcohol is well adapted for use in motor and aeroplane engines. "Solidified alcohol" is pro-

duced by the addition of cellulose esters (760) to alcohol; it is used for cooking.

ORGANIC ACIDS

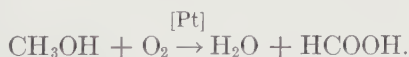
755. The Fatty Acids. — The acids of this homologous series owe their name to the fact that some of the members are constituents of animal fats and animal and vegetable oils. The *general formula* is $C_nH_{2n}O_2$, or $C_nH_{2n+1}.COOH$. The radical ($COOH$) is called the **carboxyl group** and is characteristic of organic acids. The acids of the fatty series are monobasic, so the general formula might be written $R.COOH$, in which R stands for a univalent radical. They may be regarded as derivatives of the paraffins, the alcohols, or the aldehydes:

Paraffins	Alcohols	Aldehydes	Acids
$H.CH_3$	$HCH_2.OH$	$H.CHO$	$H.CO.OH$
$CH_3.CH_3$	$CH_3.CH_2.OH$	$CH_3.CHO$	$CH_3.CO.OH$

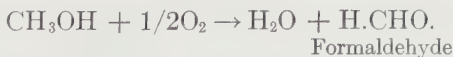
Palmitic acid, $C_{16}H_{32}O_2$, or $C_{15}H_{31}COOH$, and stearic acid, $C_{18}H_{36}O_2$, or $C_{17}H_{35}COOH$, belong to the same series as formic acid ($HCOOH$) and acetic (CH_3COOH); they are found in combination in animal fats (tallow and lard).

756. Formic Acid, CH_2O_2 or $HCOOH$. — This acid is the first member of the fatty series; it occurs in nettles, ants (Lat. *formicae*), etc. The sting of the ant, bee, and nettle is due, at least in part, to the presence of formic acid.

Formic acid can be formed by the oxidation of methyl alcohol by means of platinum (catalyst):



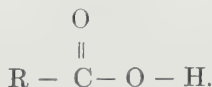
The first oxidation product of an alcohol is an aldehyde:



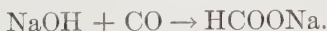
The general formula of an aldehyde is, therefore, $R.CHO$, or



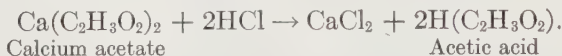
and that of the corresponding acid,



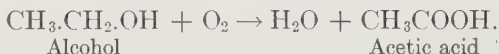
Formic acid is a colorless liquid with a pungent, irritating odor. When treated with concentrated sulfuric acid, it yields carbon monoxide and water. The salts of the acid are called **formates**: *e.g.*, HCOONa , sodium formate. This salt may be obtained by passing CO over heated NaOH :



757. Acetic Acid, $\text{C}_2\text{H}_4\text{O}_2$, or CH_3COOH . — Acetic acid occurs in combination with alcohols in the oils of many plants. It may be obtained from pyroligneous acid (731). The acid is first converted into *calcium acetate* by absorbing its vapor in milk of lime. The salt is treated in copper vessels with an equivalent amount of hydrochloric acid, and the acetic acid distilled off:



When fruit juices (cider, weak wine, etc.) or beers are left exposed to air, they soon become sour, because of oxidation of alcohol to acetic acid:



This oxidation is brought about by the agency of "mother of vinegar," or acetous ferment (*Mycoderma aceti*), a low order of plant. Vinegar, then, is essentially a dilute solution of acetic acid; it also contains coloring matter and other substances.

Acetic acid is now produced on a large scale by a synthetic method. We have seen that acetylene in the presence of a suitable catalyst combines with water to form acetaldehyde, CH_3CHO (759). This compound in the presence of the catalyst manganese sulfate unites with oxygen to form acetic acid:



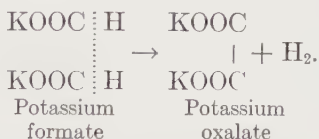
The acid flows out of the reaction chamber like soft ice. Large quantities of calcium carbide are manufactured at Shawinigan Falls, Canada, and acetic acid on an industrial scale is produced from the acetylene derived from the carbide.

Pure acetic acid (hydrogen acetate) is a white, colorless, crystalline solid, which melts at 16.5° and boils at 118° ; it has a penetrating smell and a sour taste. The compound mixes with water in all proportions, and its aqueous solution is a weak acid:



The salts of acetic acid are called **acetates**. Lead acetate or "sugar of lead," $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$, is soluble in water; it has a sweet taste, and is very poisonous.

758. Other Organic Acids. — **Oxalic acid**, $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, occurs in nature in certain plants, chiefly in species of *oxalis*, in the form of potassium hydrogen (KHC_2O_4), or calcium salt. The acid can be produced by the oxidation of many organic substances. Thus, it may be formed by oxidizing sugar with concentrated nitric acid. The acid also may be obtained in the form of a salt by heating a formate of an alkali metal:



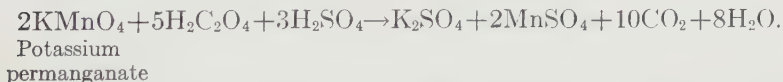
Oxalic acid is a fairly strong, dibasic acid, which may be regarded as containing two carboxyl groups:



It forms white crystals containing two molecules of water of hydration. Only the oxalates of the alkali metals and of magnesium are soluble in water. *Calcium oxalate*, CaC_2O_4 , is insoluble in water and in acetic acid, but readily soluble in hydrochloric or nitric acid.

On warming oxalic acid with concentrated sulfuric acid, it decomposes, yielding water, carbon dioxide, and carbon monoxide (438).

Oxalic acid reduces permanganate solutions:



This reaction is of value in volumetric analysis (why?). The oxalate-ion (C_2O_4^-) is poisonous.

Tartaric acid, $\text{H}_2(\text{C}_4\text{H}_4\text{O}_6)$, is a dibasic acid which occurs in nature, partly free and partly as its acid potassium salt ($\text{HKC}_4\text{H}_4\text{O}_6$) in many fruits, especially in the sap of the grape.

Tartaric acid forms colorless, monoclinic crystals, and is readily soluble in water. Its salts are called **tartrates**. "Cream of

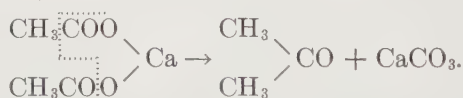
tartar" ($\text{KHC}_4\text{H}_4\text{O}_6$), "Rochelle" salt ($\text{KNaC}_4\text{H}_4\text{O}_6$), and "tartar emetic" ($\text{K}(\text{SbO})\text{C}_4\text{H}_4\text{O}_6 \cdot \frac{1}{2}\text{H}_2\text{O}$) are the most important tartrates.

759. Aldehydes and Ketones. — We have just seen that an aldehyde is the first oxidation product of an ordinary alcohol, such as methyl or ethyl alcohol (756).

Formaldehyde, $\text{H}.\text{CHO}$, is obtained by passing a mixture of the vapor of methyl alcohol and air over a hot platinum or copper spiral. It is a colorless, pungent gas, and very soluble in water. The 40 per cent aqueous solution is known as "formalin." Formaldehyde is used as a disinfectant, for preserving anatomical specimens, for hardening gelatins (*e.g.*, in the manufacture of leather), and for the production of *bakelite*.

Acetaldehyde, $\text{CH}_3.\text{CHO}$, is the corresponding aldehyde obtained from ethyl alcohol (754).

Acetone, $(\text{CH}_3)_2\text{CO}$, is the most important and common of the class of compounds termed **ketones**. It may be obtained from crude wood spirit (427) and by the dry distillation of calcium acetate, $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$:



Acetone also is produced on a large scale by the fermentation of carefully sterilized corn mash or potato-starch. It is inoculated with spores of Weizmann bacteria, which ferment starch to normal butyl alcohol and acetone. This is an extraordinary example of biological engineering. In conducting the process, air must be excluded and foreign organisms prevented from gaining access to the starch. The corn mash circulates through pipes previously sterilized by high-pressure steam, and the circulating pumps have pistons which pass through loose packings wet with a solution of carbolic acid. A single spore of the necessary micro-organism may be isolated, and from this a pure culture is obtained in sufficient quantity to ferment the contents of very large vats.

Acetone is a colorless liquid of a peppermint-like odor, and boils at 56° . It mixes with water in all proportions and is an excellent solvent for organic compounds.

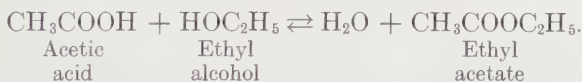
The ketones are characterized by the $=\text{CO}$ group, which is not in direct combination with hydrogen.

Bakelite is a synthetic product formed from formaldehyde and phenol or carbolic acid ($\text{C}_6\text{H}_5\text{OH}$). These substances under cer-

tain conditions form a resin-like material, which solidifies or hardens by application of heat. It is practically infusible, insoluble, impervious to water, and chemically inert. When pure, it is transparent and "amber-like" in appearance. Bakelite is a non-conductor of electricity and has great mechanical strength. It is used as an insulator, pipe stems, cigar holders, pump valves, beads, camera cases, etc.

ESTERS AND SOAP

760. Esters. — These compounds are formed by the interaction of an alcohol and an acid, just as salts are formed by the interaction of a base and an acid; hence esters are often called *alkyl salts*, *i.e.*, salts containing alcoholic radicals. In the case of an organic acid, the alkyl radical may be regarded as replacing the hydrogen of the carboxyl group ($-\text{COOH}$). Thus, ethyl acetate may be formed by the interaction of acetic acid and ethyl alcohol:



This reaction is reversible, and the equilibrium may be displaced to the right by adding concentrated sulfuric acid (why?). The action to the right is known as **esterification**, and the one to the left is **hydrolysis**. Water, then, has a tendency to hydrolyze esters. *The most characteristic reaction of esters is the splitting action of hydrolytic agents.* Esters, unlike inorganic salts, do not ionize in water.

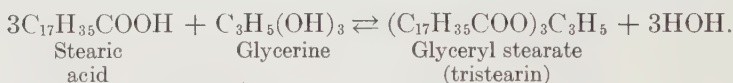
Ethyl acetate may serve as the type of this class of compounds. It is a colorless liquid, possessing a "fruity smell," and for this reason it is used in perfumery. Esters occur in plants, forming the sweet-smelling ethereal oils, such as the oil of wintergreen (753). They are therefore manufactured for use in perfumes and fruit essences.

Other fatty acids also form esters; also, inorganic acids. Alcohols containing more than one hydroxyl group may be substituted for the alcohols belonging to the series containing ethyl alcohol. Thus, *glyceryl nitrate* ("nitroglycerine") is formed when glycerine, $\text{C}_3\text{H}_5(\text{OH})_3$, is treated with nitric acid (389). Glyceryl trinitrate is an ester of the alcohol glycerine and nitric acid — an inorganic acid.

The higher fatty acids, such as palmitic and stearic, occur in

fats in combination with glycerine; or, to put it another way, **fats** (*e.g.*, tallow) are mixtures of esters of glycerine. In general it may be stated that animal fats and animal and vegetable oils are mixtures of the esters of glycerol (glycerine). The principal components of fats and oils are *tripalmitin* and *tristearin*, which are solid at ordinary temperatures, and a liquid ester, *triolein*, which is the glycerol ester of oleic acid ($C_{18}H_{34}O_2$, or $C_{17}H_{33}.COOH$). Oleic acid contains two atoms less of hydrogen than stearic acid ($C_{18}H_{36}O_2$), and for this reason it is an unsaturated acid, belonging to a different series. Now, tallow is chiefly tristearin and tripalmitin, while lard (a softer fat) contains a considerable quantity of triolein. Butter contains the same esters, as well as glyceryl butyrate (*butyrin*). Esters which hydrolyze to form glycerine are called **glycerides**.

The formation of one of the higher esters occurring in fats may be represented thus:



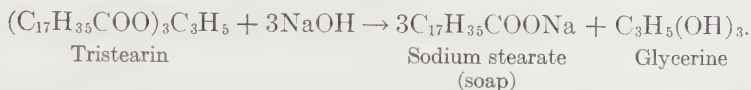
Tristearin is an ester which is abundant in beef and mutton tallow. The reaction showing its formation is reversible; therefore, when tristearin is treated with steam under pressure, the fatty ester is hydrolyzed, forming stearic acid and glycerine. Fats are thus hydrolyzed, and the fatty acids formed are used in the manufacture of candles, and the important by-product glycerine is obtained.

Oleomargarine is an artificial butter produced by churning the softer fats from cattle or hogs with a little oil (*e.g.*, cottonseed) and milk. When properly made, it is wholesome.

When cellulose (*e.g.*, cotton) is treated with acetic acid in the form of its anhydride, $(CH_3CO)_2O$, cellulose acetate is obtained. *The cellulose acetates are less inflammable than the nitrates, and are therefore used in the production of motion picture films.* They also are used in the manufacture of goggles and gas masks, and as a coating for aeroplane wings, etc. They have the advantages of being practically non-inflammable, waterproof, transparent, and non-conductors of electricity.

761. The Manufacture of Soap. — *Soaps are metallic salts of fatty acids.* In practice soaps are confined to sodium or potassium salts of fatty acids containing ten or more carbon atoms. Sodium soaps are hard, while potassium soaps are soft. We have just

seen that an ester may be hydrolyzed by treatment with superheated steam, or steam under pressure. If sodium hydroxide or potassium hydroxide be substituted for steam, the fat is hydrolyzed (*saponified*, Lat. *sapo*, soap + *facere*, to make), and a salt of the alkali metal is obtained along with glycerine:



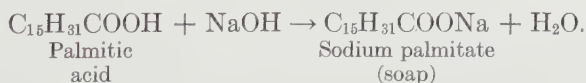
Sodium stearate is a simple soap. As a matter of fact, when fats are treated with a caustic alkali, a mixture of sodium or potassium salts is obtained.

The names and formulae of the more important members of the fatty acid series and of the corresponding glycerides involved in the manufacture of soap are as follows:

<i>Acid</i>	<i>Glyceride</i>
Lauric, $\text{C}_{11}\text{H}_{23}\text{COOH}$	Laurin, $(\text{C}_{11}\text{H}_{23}\text{COO})_3\text{C}_3\text{H}_5$
Myristic, $\text{C}_{13}\text{H}_{27}\text{COOH}$	Myristin, $(\text{C}_{13}\text{H}_{27}\text{COO})_3\text{C}_3\text{H}_5$
Palmitic, $\text{C}_{15}\text{H}_{31}\text{COOH}$	Palmitin, $(\text{C}_{15}\text{H}_{31}\text{COO})_3\text{C}_3\text{H}_5$
Stearic, $\text{C}_{17}\text{H}_{35}\text{COOH}$	Stearin, $(\text{C}_{17}\text{H}_{35}\text{COO})_3\text{C}_3\text{H}_5$
Oleic, $\text{C}_{17}\text{H}_{33}\text{COOH}$	Olein, $(\text{C}_{17}\text{H}_{33}\text{COO})_3\text{C}_3\text{H}_5$
Linoleic, $\text{C}_{17}\text{H}_{31}\text{COOH}$	Linolein, $(\text{C}_{17}\text{H}_{31}\text{COO})_3\text{C}_3\text{H}_5$
Ricinoleic, $\text{C}_{17}\text{H}_{32}(\text{OH})\text{COOH}$	Ricinolein, $(\text{C}_{17}\text{H}_{32}\text{OH.COO})_3\text{C}_3\text{H}_5$

The last three acids are unsaturated (728).

Soaps can be produced by neutralizing one of the fatty acids with a base. Thus:



In America, soap is most commonly manufactured by saponifying fat or oil with sodium hydroxide ("lye"). The "stock," or mixture of glycerides, is brought to the top of a huge kettle by means of a pipe. Lye and water are also brought to the kettle until it is filled. A single kettle will hold "stock" enough to yield hundreds of thousands of pounds of soap (Fig. 209). Steam is blown in at the bottom of the kettle and its contents are thoroughly agitated and boiled until a pasty mass of soap is obtained. In the next operation common salt is added, which causes the globules of glycerine and water to sink to the bottom of the kettle and the clear soap curd to form a layer on top (why?). The water and glycerine are withdrawn from the bottom. The soap curd, after



Courtesy of The Procter and Gamble Co.

FIG. 209. SOAP-KETTLES.

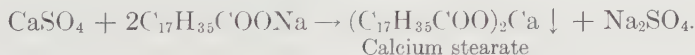
Each kettle extends two floors below that shown and has a water capacity of about three hundred thousand pounds.

purification, is pumped into large stirring bowls, or "crutchers," where it is stirred until smooth. Coloring matter, perfumes, medicinals, fillers, etc., may be added. To produce floating soap air is beaten into it by means of very large egg-beater mechanisms.

The **Twitchell process** is also employed for the hydrolysis of fats and oils. This is a catalytic process, the fat or oil being heated with water and a strong acid (catalyst). The fat or oil is boiled with sulfuric acid and the "saponifier," or "Twitchell reagent," which is obtained by treating oleic acid and naphthalene with sulfuric acid. The catalyst promotes the miscibility of oil and water. The free fatty acids which are formed by hydrolysis of the esters may be transformed into soap by treating them with sodium carbonate, which is cheaper than sodium hydroxide. The process is an economical one and can be employed in producing soap from low-grade fats or grease. It is extensively used, especially in certain European countries, such as Germany and the Scandinavian countries.

Soaps are salts of strong bases and weak acids, so in the presence of water they undergo partial hydrolysis, and have therefore an alkaline reaction. A soap interacts with the calcium and magnesium salts contained in hard waters, forming insoluble salts, such as calcium stearate and calcium palmitate.

Taking sodium stearate as a representative soap, the chemical change occurring when water containing in solution calcium sulfate interacts with the soap, is as follows:



The cleansing power of soap depends upon the fact that it is able to emulsify grease or oil, and to adsorb the dirt, such as soot (carbon). The grease and dirt may therefore be removed or washed away. A solution of soap in water is more or less colloidal.

762. Hydrogenation of Oils. — Hydrogen, in the presence of certain catalysts, may be added chemically to unsaturated carbon compounds, such as liquid fats and oils. This process is known as *hydrogenation*. We have just seen that oleic acid is an unsaturated acid, i.e., its molecule contains two atoms less of hydrogen than does stearic acid; also, that triolein is a liquid fat, because it is an ester of an unsaturated acid. Now, cottonseed oil, as well as other similar oils, contains esters of unsaturated acids. When such oils are treated with hydrogen in the presence of catalysts

(*e.g.*, nickel or nickel oxide), the hydrogen enters into chemical union with the oil, converting it into a solid fat. The manufacture of solid fats, or the chemical hardening of animal and vegetable oils, is a growing industry.

Soap made from cottonseed oil is soft and easily becomes rancid; but when the oil is hydrogenated excellent soap can be produced from it. Important soap stocks are now obtained by the hydrogenation of fish and whale oils.

EXERCISES

1. Explain the difference between a carbohydrate and a hydrocarbon. Name the three general classes of carbohydrates. Classify the following: Glucose, dextrin, maltose, glycogen, and gums.

2. Give the occurrence, preparation, and properties of sucrose. Explain the meaning of "invert sugar." Explain just what occurs when yeast is introduced into a dilute solution of ordinary sugar.

3. What is glucose and how is it manufactured? What are its properties and uses? Explain the fermentation of a solution of glucose. What is Fehling's solution and for what is it used?

4. Give the chief sources of starch. What are the properties of starch? How may it be separated from gluten? What chemical changes does starch undergo during the process of digestion? How may dextrin be prepared?

5. Give the sources, composition, properties, and uses of cellulose. Outline methods for the following: (1) the manufacture of nitrocellulose; (2) the manufacture of celluloid; (3) the conversion of cellulose into glucose.

6. Define the term, alcohol. Show that glycerine is an alcohol. Describe the manufacture of methanol. What are its properties and uses?

7. Describe the manufacture, including the chemical equations, — of (1) ethyl alcohol from molasses, and (2) from starch. What are enzymes and how do they act? Name some enzymes which take part in the digestion of food.

8. Starting with calcium carbide, show how ethyl alcohol can be synthesized.

9. How may ethyl alcohol and methyl alcohol be recognized?

10. Explain the meaning of "fatty acids." Write down the names and formulae of several of them, and show the relation of a fatty acid to the corresponding paraffin, alcohol, and aldehyde.

11. Give the sources of formic acid, write its structural formula and that of formaldehyde. Write the formulae of sodium formate and lead formate. How may carbon monoxide be prepared from a formate? How may potassium formate be prepared?

12. How may acetic acid be prepared from wood and from alcohol? Explain how cider changes into vinegar. What are the properties of acetic acid? What action, if any, has water upon aluminium acetate? Explain. Mention the uses of some acetates.

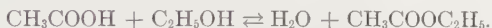
13. Explain, and also illustrate, the formation of esters. State a very characteristic property of an ester. Mention some esters which occur in fats and oils. How do esters differ from ordinary salts?

14. Explain and illustrate fully the hydrolysis of esters. What are soaps and how are they ordinarily prepared from fats?

15. Outline the Twitchell process. What are some of its advantages?

16. Explain why an aqueous solution of a soap has an alkaline reaction. Explain how soap removes grease and dirt from a material.

17. (a) Apply the law of molecular concentration (214) to the reaction expressed by the following equation:



(b) If a mol of acetic acid and one of alcohol were mixed, and equilibrium established when two-thirds of a mol of the ester is formed, find the numerical value of the equilibrium constant.

(c) If 4 mols of alcohol were added to 1 mol of acetic acid, what should be the yield of ester at equilibrium?

18. From a given amount of acid (or alcohol) show how the maximum quantity of ester may be obtained.

19. How may certain oils be converted into solid fats?

20. What products are obtained when the following classes of compounds are burned: (1) hydrocarbons; (2) carbohydrates; (3) alcohols; (4) esters (oils and fats)? Illustrate fully by means of chemical equations.

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CHAPTER XLII

THE FOOD OF PLANTS AND OF ANIMALS

THE FOOD OF PLANTS

763. **Introductory.** — Agriculture is the basic industry of mankind. The fundamental wealth of a great country, such as America, lies in the fertility of its soil. Since all human progress is so dependent upon the conservation and enrichment of the soil, it is important to devote special attention to these matters.

Plants, in their growth, are able to utilize the lifeless, inorganic materials found upon the surface of the earth, whilst animals are dependent either directly or indirectly upon plants. A tree, for instance, stands in the same place, perhaps for centuries, receiving its food from the air and soil, the former supplying carbon dioxide and water and the latter inorganic salts. The foods required by plants are rather simple as compared with those utilized by animals. Plants have a much greater synthetic power than animals. Thus, they have the ability to synthesize starch and cellulose from carbon dioxide and water, and proteins from ammonium nitrate and other substances.

The ultimate source of our food is plants, which in turn are produced in nature's laboratories exclusively from soil, air, water, and sunshine. In the growth of farm crops, only thirteen elements out of the ninety known ones appear to be necessary: namely, hydrogen, oxygen, carbon, nitrogen, chlorine, potassium, sodium, calcium, magnesium, iron, phosphorus, silicon, and sulfur. Only five of these are metals. Hydrogen, oxygen, and carbon make up the bulk of the plant, being freely supplied by the air and water. The other elements are supplied in the form of their salts, and are assimilated from the soil by means of the roots of plants. *In general, for most green plants, the salts of potassium, calcium, magnesium, and iron, supplied in the form of nitrates, sulfates, and phosphates, together with carbon dioxide and water, are usually adequate for complete growth and reproduction.*

Protoplasm, a very complex, jelly-like mixture, is the basis of the cells of organisms. It is composed of substances containing carbon, hydrogen, oxygen, nitrogen, and other elements, being somewhat similar in composition to albumin, or the white of egg.

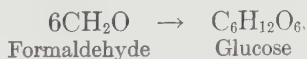
Protoplasm circulates in the cells of plants as well as animals. *Chlorophyll*, the green coloring matter in plant cells, is also a very complex material. Without it the higher orders of plants are not able to feed upon inorganic matter. Non-green plants, such as fungi and mildew, procure their food from other sources, such as dead organic matter. Magnesium is an essential constituent of chlorophyll, and iron is in some way associated with its formation. It is well known that when green plants are deprived of iron the leaves turn pale green or yellow, but health may be restored by adding iron to the soil or by spraying the leaves with salts of iron.

764. Photosynthesis. — When a green plant is exposed to sunlight, certain rays are absorbed, and in the presence of the little bodies called *chloroplasts* important carbon compounds are synthesized from the carbon supplied by the carbon dioxide of the air. This process is called *photosynthesis*. Carbon dioxide and water are very closely related to plant life, for they are the raw materials from which plants are able to synthesize such carbohydrates as cellulose, starch, and sugar. The formation of the carbohydrate glucose, a simple sugar, may be represented thus:



Professor Willstätter of Munich has made the interesting discovery that the chlorophyll of plants and the hemoglobin of blood may be regarded as being derived from a common substance, namely, *aetioporphyrin* ($\text{C}_{31}\text{H}_{36}\text{N}_4$). By chemical treatment of chlorophyll and of hemoglobin Willstätter is able to produce aetioporphyrin. Chlorophyll is a complex magnesium compound, while hemoglobin contains iron. It is noteworthy that chlorophyll releases oxygen from carbon dioxide, whilst hemoglobin takes up oxygen. It is also interesting to know that Willstätter has studied many flowers of variegated colors, and he finds that these colors have as their basis a common substance, namely, *cyanidine*.

The simplest carbohydrate capable of being formed by the action of a single molecule of carbon dioxide upon a molecule of water is *formaldehyde* (CH_2O). It is of much interest to note that formaldehyde has been found in plant tissues. In photosynthesis there is evidence that formaldehyde is formed and that six molecules of this compound come together to form a molecule of a simple sugar, such as glucose:



E. C. C. Baly, an English chemist, succeeded in 1924 in producing formaldehyde by exposing carbon dioxide and water to ultra-violet light. When the solutions in which aldehyde is produced are made slightly alkaline, a syrup is obtained, which contains sugars very similar to those occurring in plants. Some day an abundant supply of sugar may be produced by synthetic methods. The fundamental fact of photosynthesis is that plants are able to convert carbon dioxide and water, which have no fuel value or energy value for life, into carbohydrates which possess a high fuel value, and are therefore available for the production of energy in organisms. Solar energy is stored up in the form of food and fuel.

Experiments have been carried out to determine the effect of artificial light upon the growth of plants; but no artificial light has been found that compares with sunlight in both intensity and quality (Fig. 210). Chlorophyll is green because the green part of the spectrum is least absorbed, which suggests that it may be the red portion of the spectrum that is most effective in photosynthesis. It has been observed that when sunlight is employed as the source of light, photosynthesis is most marked in the red part of the spectrum. As the result of carefully conducted experiments, Fritz Schanz has concluded that light of short wavelengths, and especially ultra-violet rays, are detrimental to the growth of plants. Schanz therefore recommends for use in green-houses a yellow glass (*Euphos glass*) which cuts off the ultra-violet rays.

It should be added, however, that the intensity of the ultra-violet rays reaching the earth's surface is relatively low.

Scientists have also conducted experiments to determine the effect on growing plants of increasing the carbon dioxide concentration of the air. At Essen, Germany, for instance, flue gases were purified and the resulting carbon dioxide piped into fields of sugar-beets. It is reported that there was an improved growth and yield of beets.

The process of respiration is characteristic of all living things, whether animals or plants; and so far as we know all living plants give off carbon dioxide as do animals. Green plants absorb carbon dioxide in sunlight and give it off in darkness.

765. The Ashes of Plants. — Knowledge as to the nature of inorganic compounds required for the growth of plants is obtained by burning the plants and analyzing the ashes. *Analysis of the ash of the rye plant*, for example, shows its composition to be as follows:



Courtesy of Arthur, Webster and Guhrle.

FIG. 210. EFFECT OF ARTIFICIAL LIGHT ON TOMATO PLANTS

From left to right, 5, 7, 12, 17, 19, and 24 hours of artificial light in each twenty-four-hour period. Control grown in greenhouse at same temperature and humidity.

	<i>Per cent</i>
Potash salts.....	37.16
Sodium chloride.....	0.76
Lime and magnesia.....	12.32
Oxide of iron.....	0.50
Phosphoric acid.....	20.35
Sulfuric acid.....	4.03
Silica.....	24.88
	<hr/>
	100.00

In order, therefore, for such a plant as rye to grow, all these components must be in the soil. The ashes of other plants vary more or less in composition. Some of these components, such as oxide of iron and silica, are always available in abundance in the soil, whilst others are not. About 1840, Liebig showed for the first time that the soil will become exhausted unless phosphoric acid (as soluble phosphates), nitrogen (usually as nitrates or ammonium salts), and potash salts are supplied to it; hence the use of *artificial fertilizers*. Liebig discovered the connection between soil and crops, or the principle "to give back to the soil by artificial means those substances which are removed by the growth of plants."

766. Nitrogen. — It is to be observed (765) that the analysis of plant-ashes gives no information as to nitrogen, because the compounds of nitrogen are volatilized either unchanged or in combination with other elements when the plants are burned.

The "cycle" of nitrogen has been discussed (359). Plants require nitrogen for the synthesis of proteins, but they cannot assimilate nitrogen by their leaves as they do carbon dioxide. In general, it may be stated that, nitrates and ammonium compounds are the only sources of nitrogen for the majority of green plants. It is estimated that a ton of wheat takes from the soil about 47 pounds of nitrogen. Sir William Crookes, in addressing the British Association for the Advancement of Science, in 1898, stated that the world was nearing the limit of wheat production, and suggested as a solution of the problem the use of more fertilizer to increase the yield of grain per acre, especially fertilizers obtained by the fixation of atmospheric nitrogen (377). It is interesting to note that England has increased the average yield of wheat from 6 to 32 bushels per acre in the last 700 years, a part of this increase being due to fertilization. Belgium and Germany produced (1913) 35 bushels per acre, but in 1913 the average production in the United States was only 15 bushels.

The chief nitrogenous fertilizers are sodium nitrate (Chile saltpeter), calcium nitrate, ammonium sulfate, and calcium cyanamide.

Nitrogen also is supplied by the decay of nitrogenous organic matter. Plant and animal residues are destroyed by bacteria, some of which produce ammonia, a portion of which is transformed by soil bacteria, first into nitrites and then into nitrates. Bacteria may reverse the process, *i.e.*, change nitrates into nitrites:



Ammonia and nitrites may also be transformed into atmospheric nitrogen. Only a small amount of nitrates is found in the soil or ground waters at any one time, due to the fact that nitrates are easily reducible.

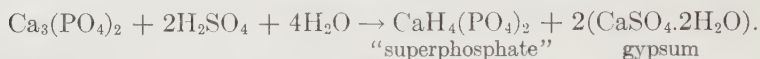
The soil is enriched by the growth of **leguminous plants**, such as clover, alfalfa, peas, and beans. It was known before the Christian era that the yield of grain could be increased by growing a leguminous crop on a field the year before grain was produced. The principle of **crop rotation** is a very valuable one in farming. In the case of leguminous plants the symbiotic bacteria living on the nodules of the roots bring about the synthesis of proteins and related materials, the nitrogen for this purpose being taken up from the air. The complex proteins may ultimately yield nitrates, which are available as plant food.

767. Potassium. — Potassium is another soil element essential for the growth of plants, for without an adequate supply of it the general tone and vigor of the plants are lowered. Potassium is not a constituent of carbohydrates, but in some mysterious way it is intimately associated with their production; hence the popular saying, *potash makes starches and sugars*. Potash is of great importance in the growth of sugar-beets, potatoes, etc. In case of potash starvation the vigor of the plant is much reduced, and it is more susceptible to attack by parasites. Potash was originally obtained as potassium carbonate by treating plant-ashes with water. This partially explains why wood-ashes are useful as fertilizer. Potash salts were expensive until 1860, or until the great Stassfurt deposits were utilized. Before the war Germany was producing potash salts (calculated as K_2O) at the rate of about one million tons per year. The chief potassium salt obtained from these deposits is the chloride (KCl); it is extensively used as a fertilizer. Considerable potassium sulfate (K_2SO_4) also is em-

ployed as a fertilizer. We have seen that potassium compounds are supplied to the soil by the weathering of potash feldspar (451).

768. Phosphoric Acid. — Phosphorus is of the highest importance in the growth of plants. The exact function of this element in plant-nutrition is not understood, but *an adequate supply of phosphorus stimulates the development of the roots and hastens the process of ripening*. It is especially abundant in the seeds of plants; hence the saying, *phosphorus makes seeds*.

Phosphoric acid is supplied to plants in the form of soluble phosphates (413). Phosphates are obtained from bones, phosphorite (403), and by dephosphorizing iron (Thomas' phosphate powder). Since normal calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$, is almost insoluble in water, it is treated with sulfuric acid in order to secure "superphosphate" (primary calcium phosphate):

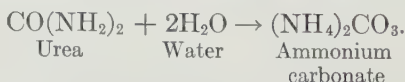


This mixture of superphosphate and gypsum is sold under the name of "superphosphate of lime." It is used on an enormous scale as a fertilizer.

Sir John Lawes discovered in 1840 that when bone meal or phosphate rock is treated with sulfuric acid, the product is much more effective than is the untreated material, in the growth of plants.

Salts used as fertilizers must not be too highly soluble in water, for they are too readily washed away. We shall learn (see Colloid Chemistry) that potash compounds, ammonium salts, soluble phosphates, etc., are adsorbed by the soil, *i.e.*, the fine particles of the soil are able to hold these salts upon their moist surfaces.

769. Manure. — Barnyard manure is very helpful in the fertilization of many plants. A ton of manure usually contains about six pounds each of potash and phosphoric acid, and eight pounds of nitrogen (chiefly as urea and proteins). Bacteria play an important rôle in the transformation of manure. Urea, for instance, is transformed by an enzyme into ammonium carbonate:



The smell of ammonia is very common around barnyards; for ammonium carbonate is unstable, one of the products of decomposition being ammonia.

James B. Sumner of Cornell University has isolated the enzyme (*urease*) which converts urea into ammonium carbonate. He obtained it from the jack bean. It was prepared in the form of octahedral crystals, and is a protein. Urease is the first enzyme to be prepared in the pure state.

It may be that synthetic urea will be the chief nitrogenous fertilizer of the future. The proteins and similar bodies yield ammonia. When manure is scattered on the ground, soil bacteria assist in the oxidation of ammonia to nitrates.

770. Indirect Fertilizers. — Some substances which are added to the soil are not assimilated by the growing plants. Thus, gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, is employed extensively as an indirect fertilizer (about 100 pounds per ton of manure). The salt is very sparingly soluble in water, but it interacts with the ammonium carbonate produced from the urea, forming ammonium sulfate and calcium carbonate:



Ammonium sulfate is much more stable in the manure and soil than is ammonium carbonate (why?), and calcium carbonate is only slightly soluble. While gypsum "fixes" the ammonia of manure piles, slaked lime would liberate it (why?).

Lime and limestone (calcium carbonate) transform the insoluble phosphates of aluminium and iron into more soluble phosphates of calcium.

The *acidity of a soil* may be neutralized by the addition of air-slaked lime or calcium carbonate. Soils may be naturally sour, or the acidity may be brought about by the use of too much fertilizer in the form of sulfates (*e.g.*, $(\text{NH}_4)_2\text{SO}_4$).

771. Soil Bacteria. — There are many kinds of micro-organisms in the soil, bacteria being numerically the most important component of the soil micro-flora. It is now well known that micro-organisms play a major part in the production and maintenance of vegetation. The processes of decay, putrefaction, and fermentation, so important on the farm, are closely related to micro-organisms. The soil consists of innumerable earthy particles of varying sizes, each particle being surrounded by a thin layer of moisture. Within this film of moisture there are active micro-organisms, which play an important rôle in the growth of plants. The soil contains a mixture of culture media, which are ordinarily principally found within the five or six inches of the surface soil.

According to J. G. Lipman, the average acre of cultivated land

contains in the humid region something like 20 tons of organic matter, which is constantly being attacked by micro-organisms, carbon dioxide, water, nitrates, sulfates, etc., being produced. While ammonia is produced, it does not accumulate in the soil, for it is oxidized to nitrous and nitric acids, the final product in the soil being a nitrate, most commonly calcium nitrate. This natural process of *nitrification* is of great importance, and is brought about by the agency of soil bacteria. The rôle played by symbiotic bacteria in the fixation of atmospheric nitrogen has already received consideration. It is estimated that cow-peas during a season of growth fix from 10 to 15 pounds of nitrogen per acre, while alfalfa or sweet clover may fix from 200 to 300 pounds of the element per acre. By plowing under clover, the soil is greatly enriched.

Science has devised ways and means for a certain amount of control over soil bacteria. For instance, such chemicals as formaldehyde, carbon disulfide, and copper sulfate are sometimes employed to rid soils or seeds of a large part of their micro-organisms. Greenhouses are quite commonly disinfected with formaldehyde or carbon disulfide. Soil-inoculation is now not an uncommon practice. This means that large numbers of specific organisms are introduced into the soil in order to accomplish certain ends. Soil micro-organisms play the important part of restoring to circulation the elements locked up in plant and animal life.

772. Plant Pests and Diseases. — Plants are subject to many kinds of diseases and pests. According to Lord Bledisloe, from 15 to 20 per cent of the world's crops are lost through insects and fungoids; and it is estimated that the farmers of the United States spent \$1,600,000,000 in the year 1925 to combat insects and grubs.

Insects which prey upon plants may be divided into two classes — *sucking insects* and *chewing insects*. The former puncture the plant or its fruit in order to obtain the juice, while the latter eat the foliage.

As a rule, insecticides and fungicides are chemical compounds or mixtures of compounds. **Insecticides** are divided into *poison sprays*, or *stomach poisons*, and *contact poisons*. The former kill when taken internally, while the latter destroy life by mere contact. Poison sprays usually contain some form of arsenic compound. Finely divided lead arsenate in suspension in water is used on a very large scale and is exceedingly effective. Calcium arsenate is cheaper than lead arsenate, and is employed for fighting

the boll-weevil, so destructive to the cotton-plant, and the potato-beetle. The cotton-plant is dusted with calcium arsenate in the form of very fine powder dropped from airplanes. *Pyrethrum* is very effective as a contact insecticide. *Oil emulsions* are also extensively used. The emulsion is prepared by adding chemicals, such as fish-oil soaps, to the oil. A soap film is formed around the droplet of oil. *Nicotine*, an alkaloid occurring in tobacco, is rapid and effective. *Lime-sulfur* is very extensively employed for scale insects. It may be prepared in concentrated form by boiling together water, sulfur, and slaked lime. The solution contains sulfides. Certain **fumigants** are also employed for destroying scale insects. Thus, *hydrocyanic acid gas* (Prussic acid) is used in greenhouses and on nursery stock. The liquid compound may now be purchased in glass cylinders. It should be borne in mind that it is a most poisonous substance! *Carbon disulfide* (CS_2) finds extensive application for insects which infest stored grain or seed. Carbon disulfide, while very effective, is dangerously inflammable and is toxic to animals, so the United States Department of Agriculture now recommends for use a mixture of ethyl acetate and carbon tetrachloride. It is not inflammable, nor is it poisonous to man.

The loss from fungi is perhaps as great as that from insects. Sulfur and certain compounds containing sulfur and copper are generally employed. Sulfur was used more than a century ago for controlling mildew. *Bordeaux mixture* is very extensively employed as a fungicide, as in the growing of grapes. It is prepared by mixing a solution of copper sulfate with slaked lime.

It is now fairly common to treat seeds, before planting, with certain chemicals in order to kill fungus spores. For this purpose a solution of formaldehyde, corrosive sublimate, or powdered copper carbonate may be employed.

THE FOOD OF ANIMALS

773. Introductory. — We have seen that animals are dependent upon plants for their food; also that the food of animals, is, as a rule, much more complex than that of plants. The proteins, carbohydrates, and fats are characterized by their high molecular weights, and some of them have very complicated structures. The synthetic power of animals is very limited. They are able, however, to synthesize fats from carbohydrates.

Food may be defined as "that which taken into the body, either builds tissue or yields energy."

The body may be compared with a machine, the material of which is oxidized, in each case furnishing power and heat. There are important differences, however, between the human machine and a steam engine. The former is self-building, self-repairing, and self-regulating. The steam engine is dependent solely upon the fuel which is supplied to it, while in the human organism the reserve material may be drawn upon to supply energy. Furthermore, a portion of the food supplied to the body is utilized in its repair or growth.

There are about 15 elements in the human body, oxygen furnishing about 65 per cent.

The Constituents of Food of Man and Animals. Food of man and ordinary animals consists of the following constituents:

(1) *Proteins* (albuminous or nitrogenous foods). These form the chief constituents of lean meat, egg white, fish, the gluten of flour, etc. They build and repair tissues, and if only a little fat and carbohydrate is present, they serve as fuel.

(2) *Carbohydrates* (including starch and sugar). Serve as fuel; partially transformed into fat.

(3) *Fats* (including certain animal and vegetable oils). Serve as fuel; partially stored as fat.

(4) *Mineral Salts* (NaCl, phosphates of potassium and of calcium, etc.). Share in forming bone; assist in digestion; necessary for normal activity of tissues.

(5) *Water*. Constitutes more than two-thirds of the body.

(6) *Vitamins* (accessory food substances). These are necessary to health and growth.

(7) *Oxygen*. Oxidizes carbon and hydrogen to form energy.

According to the Food (War) Committee of the Royal Society a diet must meet the following requirements:

(1) Its calorie (energy) value must be sufficient.

(2) It must contain certain minimum amounts of adequate proteins, carbohydrates, fats, mineral salts, and vitamins.

(3) It must correspond so far as practicable to the dietetic habits of the nation.

774. The Proteins. — The word *protein* is derived from a Greek word meaning "to take the first place," because the great physiological importance of this group of substances was early recognized. Proteins are found in all living matter, and are found therefore in varying amounts in all natural foodstuffs. Since they form the

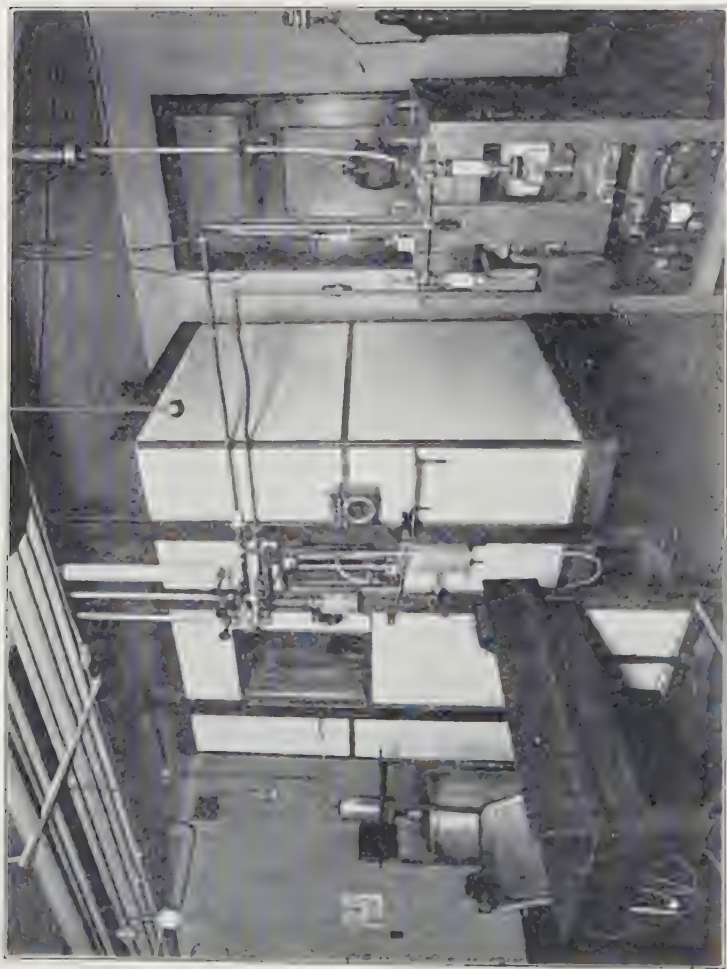
main constituents of living animal tissues, they are most plentiful in animal foods such as meat, eggs, fish, etc. Proteins are the most complicated substances which have ever been investigated, and they have very high molecular weights. *All proteins contain carbon, hydrogen, nitrogen, oxygen and sulfur, and a few contain phosphorus.* Iron, copper, manganese, zinc, and iodine are found in small quantities in certain proteins. Iodine, for instance, is found in the thyroid gland (285). The proteins are utilized mainly for building up animal tissues, but are also very useful as a source of bodily energy. For providing the material for growth in the young animal and for repairing the waste of tissues in the full-grown animal, they cannot be replaced by other foods. The animal proteins are more valuable for this purpose than are vegetable proteins. Milk is therefore of special value among proteins, particularly for the young. Animal heat may be supplied more cheaply by the substitution of carbohydrates. During digestion the giant protein molecules are hydrolyzed into simpler substances, such as the *amino-acids*. These acids contain the amino group ($-\text{NH}_2$): *e.g.*, glycine is amino-acetic acid, $(\text{NH}_2)\text{CH}_2\text{COOH}$.

775. Carbohydrates and Fats. — Carbohydrates (745) and fats (760) are the chief sources of energy. In almost every diet carbohydrates form the main source of energy, being very abundant in the temperate climates. They are by far the cheapest variety of food, and constitute the main part of vegetable foods, such as cereals, peas, and beans.

The energy value of a food is determined in a bomb calorimeter (206). Atwater and others have measured by means of the respiration calorimeter the amounts of energy evolved by foods during combustion in the body (Fig. 211). Experiment has shown that the material which is thus oxidized, yields the same amount of energy as it would if burned in the bomb calorimeter. The total quantity of energy in the form of heat and mechanical energy produced by the oxidation of the body, is equivalent to the total energy produced by oxidizing the material in the calorimeter (see Conservation of Energy).

Fats yield about 4,000 Calories per pound, carbohydrates 1,800, and proteins about 1,800. This means that a pound of fat (*e.g.*, butter) is equivalent in heat energy to a little more than two pounds of either a carbohydrate or a protein (*e.g.*, lean meat or egg albumin).

Fats are utilized mostly in the form of stearin, palmitin, and olein. Oily fats are more easily assimilated than are hard fats.



Courtesy of C. F. Langworthy.

FIG. 211. RESPIRATION CALORIMETER FOR EXPERIMENTS WITH MAN.

(Brought from Middletown, Conn., to Washington, D. C., and improved.)

Carbohydrates are more easily oxidized than fats. In order to secure complete oxidation of fat in the body, carbohydrate should be oxidized at the same time. Proteins assist the Eskimos in the complete combustion of fats. Fats are more sustaining than carbohydrates, but carbohydrates are more economical. The athlete is quickly supplied with energy after eating sugar, while a hibernating animal is sustained for a long period of time by the slow oxidation of stored-up fat. Sugar is readily absorbed from the alimentary canal, and is most useful for sustaining muscular effort. In case vigorous muscular effort has to be undertaken and sustained, it is necessary that the diet should contain not less than 25 per cent of its energy in the form of fat. Thus, the Canadian lumberman lives on a diet containing a large proportion of fat pork, the fat representing 35 to 40 per cent of the total energy of the food.

776. Mineral Matter. — To keep the body in health, it is necessary that it be supplied with an adequate amount of mineral matter. *In the case of rickets there is a marked disturbance in the assimilation of calcium and phosphorus.* These elements are especially necessary for the growing child in order that the skeleton may be properly formed. Calcium is the element which is most constant in amount in the blood. In case of rickets, the phosphorus content of the blood is below normal. Calcium and phosphorus are supplied by milk. Cheese is rich in calcium. Phosphorus is supplied by many other foods, such as eggs and meats; but in many cases the diet is deficient in calcium, as in the white bread, meat, potato, and sugar diet. Of the vegetable foods, only the leaves of plants are rich in calcium; they are also rich in vitamins. The leaves of certain plants are, indeed, a complete food. For instance, the bison, which once flourished on American plains, lived solely on grass.

777. Vitamins. — In recent years (since 1912) it has been discovered that animals require for their growth and health certain accessory food substances termed vitamins. These substances are present in traces in nearly all fresh foods. In their absence growth may cease, and various diseases, such as scurvy, beri-beri, or rickets, may be produced.

The vitamins are difficult to prepare, and their chemical nature and constitution have not been fully determined. Dr. E. V. McCollum has designated the various known vitamins by the letters of the alphabet, pending the time when their composition shall be exactly determined. They may be described as follows:

- Vitamin A: growth-producing; prevents blindness.
- Vitamin B: antineuritic; appetite-promoting.
- Vitamin C: antiscorbutic (scurvy-preventing).
- Vitamin D: antirachitic (prevents rickets).
- Vitamin E: fertility-promoting.

Vitamin A (fat-soluble A). Where there is a deficiency of this vitamin the animal fails to grow; so the vitamin is called the growth-promoting accessory food factor. It accompanies certain fats and oils, such as cod-liver oil, butter, and fat of egg yolks. It is also present in whole milk, and is especially abundant in liver, sweetbreads, and kidney. Certain green, leafy vegetables, such as spinach, lettuce, celery, and beet-tops, are especially rich in vitamin A. Children, in particular, require this vitamin. In the ordinary cooking of foods vitamin A is fairly stable; but prolonged heating in contact with air causes its oxidation and therefore its destruction. If the diet is deficient in vitamin A for a prolonged period, a disease of the eye known as xerophthalmia of dietary origin may develop, in certain cases leading to blindness. According to McCollum, a grandmother remedy long used in Japan consisted of giving the sufferers chicken livers or eel fats.

Vitamin B (water-soluble B). A lack of this vitamin leads to stunted growth and to beri-beri. It is closely related to the nervous system; hence it is called the antineuritic vitamin. Beri-beri is a disease common in Asiatic countries where the people live largely on rice. Polished rice is lacking in vitamins. For instance, when birds are fed exclusively on polished rice, symptoms (including paralysis) typical of beri-beri develop. The disease is rapidly cured, however, by feeding the birds whole rice or rice polishings. The true cause of the paralysis of the nervous system of animals was discovered in 1897 by Dr. Eijkman, of Holland. Vitamin B is relatively abundant in plants, such as unpolished rice, tubers and roots, leafy vegetables, fruits, in glandular organs of animals, and in cereal grains. It is lacking in refined mill flours and in animal and vegetable oils. Vitamin B is not readily destroyed by heating the foods in which it occurs.

Vitamin C (water-soluble C). This is the scurvy-preventing (antiscorbutic) vitamin. Scurvy was known to the Greeks and other ancient people. It has been very common in armies and navies. Captain Cook, in 1772, recognized the value of fresh food, and therefore supplied his crew with it. During his voyage of three years there was an absence of scurvy. Recognition of the

vitamin character of the substance which prevents scurvy was not accomplished, however, until 1919 to 1920. Fresh fruits and green vegetables are the chief source of vitamin C'. We may mention in particular the citrus fruits, the tomato, celery, raw cabbage, and lettuce. There is little in nuts, meats, and grains, and especially in flour and cereal foods prepared by refining methods. Vitamin C' is the least stable of the vitamins, and is liable to be destroyed when food is cooked, especially in contact with air. Pasteurized milk might lead to scurvy in the case of children unless given with orange juice or tomato juice, the latter being quite digestible and cheaper. According to Kohlman and Eddy, the antiscorbutic properties of canned fruits and vegetables may be preserved, provided they are protected from atmospheric oxygen in canning, which destroys vitamin C' by oxidation. This may be accomplished by immersing the fruits or vegetables in water, slightly salted, for a few hours, which shuts off the air and also results in the removal of the oxygen of the vegetable tissues.

Vitamin D. This is the antirachitic vitamin, or the one which prevents rickets, a disease very common to children, particularly in certain industrial districts. Children suffering from rickets have abnormal bones and are anemic. Vitamin D is most abundant in cod-liver oil, and is contained in appreciable amounts in butter and in egg yolk. Rickets do not occur in the Arctic regions where the diet is principally fish or animals which feed upon fish. It is also true that the disease is very uncommon in the tropics, where the body is subjected to strong irradiation. The very short rays, or the ultra-violet rays, are the effective ones. It is believed that the antirachitic vitamin D is a modified cholesterol. It has been discovered that irradiation with ultra-violet light causes inactive vegetable oils to take on antirachitic properties. It appears that vitamin D can be produced from a sterol. *Activated Ergosterol* is obtained. It also appears that the antirachitic potency of butter fat is owing to the consumption by the mother of irradiated food materials; and the irradiation of green vegetables, such as spinach and lettuce, increases their value as preventives of rickets.

Irradiation is now carried out by trained technologists, and vitamin D is produced on a commercial scale. Such products as *Radiostol* and *Radiostoleum* are available. The former is issued as a sweetmeat pellet, and the latter is stated to possess at least twenty times the vitamin content of the finest cod-liver oil.

It should be noted that glass does not allow the ultra-violet

rays of sunlight to pass; therefore, sunlight which has passed through glass has very little effect, if any, in preventing rickets.

H. M. Evans has discovered a fertility-promoting vitamin, which he termed *vitamin X*, but McCollum calls it *vitamin E*.

W. H. Eddy and his associates have prepared from yeast a white, crystalline substance called *bios*. It contains carbon, oxygen, hydrogen, and nitrogen. Bios is a powerful stimulant to growth; it may be vitamin B.

778. The Food Requirements of Man. — The value of a food to the body may be determined by finding its caloric value. In case the total energy given off by an individual in the course of a day is known, it suffices to supply him with a food capable of yielding the same number of utilizable calories. In reckoning the food requirements it is of course necessary to take into account waste and refuse. Under ordinary conditions this may be taken as about 10 per cent, *i.e.*, the food as purchased should have a utilizable caloric value about 10 per cent above that actually required by the individual. The energy requirement of a person depends, of course, upon his size, age, and occupation. A man at rest requires much less food than a man at work.

The Food (War) Committee of the Royal Society arrived at the following figures:

	Energy Requirements	Food Requirements
Tailor.....	2,500 ¹ Calories	2,750 Calories
Bookbinder.....	2,800 "	3,100 "
Shoemaker.....	2,850 "	3,150 "
Metal worker or Carpenter....	3,200 "	3,500 "
Painter.....	3,250 "	3,600 "
Stonemason.....	4,400 "	4,850 "
Woodcutter.....	5,000 "	5,500 "

¹ 1 Calorie = 1,000 calories.

These are the requirements for the "average man" — *i.e.*, a man from twenty-five to fifty years of age, weighing (unclothed) 145½ pounds, and 5 feet, 7.4 inches tall. In these figures 300 Calories are allowed to cover the energy expended in traveling from a man's house to his place of work, and 10 per cent to cover the difference between food as digested and food purchased. The average food requirement for the seven classes of workmen is about 3,300 Calories. The average brain worker is abundantly supplied by a diet yielding from 2,200 to 2,600 Calories, or approximately 1,000 less than the average bodily worker.

The average working woman requires about 2,650 Calories per day, while the requirement of the sedentary woman may be placed at 2,100 Calories.

The diet of the brain worker should be light and digestible and should contain relatively more protein and less fat than that of the individual who earns his living by the work of his muscles.

The protein in the diet of the "average man," doing moderate work, may be placed at about 80 g. According to the Royal Society Food Committee, the composition of the diet for the "average man," at moderate work, should be as follows:

Protein.....	70 grams	=	280 Calories
Fat.....	90 "	=	810 "
Carbohydrates.....	550 "	=	2,200 "
<hr/>			
Total.....			3,290 Calories

This refers to that part of the diet actually utilized.

The average calorific value per gram of the three classes of foods may be taken as follows: Proteins, 4 Calories; carbohydrates, 4 Calories; and fats, 9 Calories. The values per pound may be obtained by multiplying these numbers by 453.6 (the number of grams in one pound).

779. The Composition of Common Food Products.—The composition of food products varies greatly. That of some of the most common foods may be seen by reference to Fig. 212 (see the Langworthy Charts, U. S. Department of Agriculture). The caloric value per pound is also shown. Thus, white bread has a caloric value of 1,180 per pound; butter, 3,405; whole milk, 315; and beef steak (edible portion), 1,090. According to these figures, 1 pound each of white bread, milk and beefsteak, and 4 ounces of butter would yield, when burned in the body, a total of 3,436 Calories. It is quite easy to calculate from such charts, the total proteins, carbohydrates and fats supplied by a diet, and the total cost of food required to supply the bodily needs, provided the market value of each kind of food is known.

The composition of a few other common foods is given in the table on p. 795 (Langworthy).

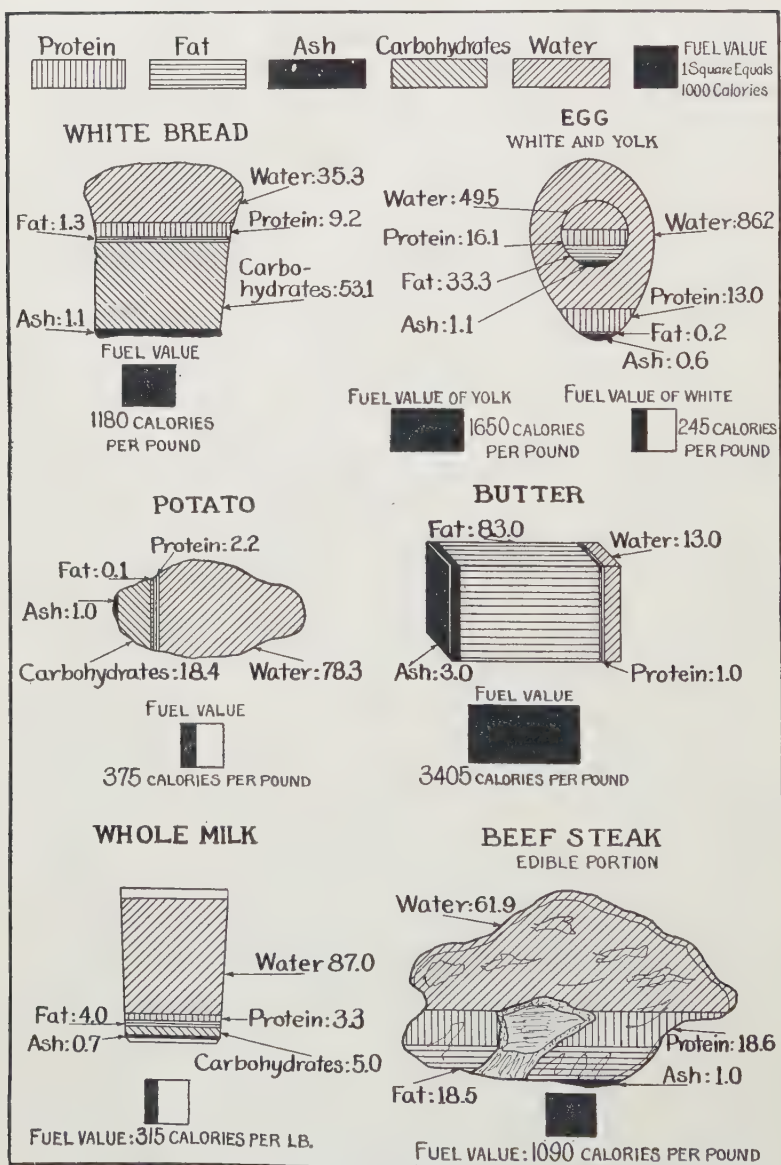


FIG. 212.

Food	Protein	Carbo- hydrates	Fat	Water	Ash	Calorific Val. per Lb.
Bacon.....	9.4	...	67.4	18.8	4.4	3,090
Oatmeal (cooked).....	2.8	11.5	0.5	84.5	0.7	280
Cream Cheese.....	25.9	2.4	33.7	34.2	3.8	1,885
Mackerel (fat fish).....	18.3	...	7.1	73.4	1.2	620
Navy Bean (dry).....	22.5	59.6	1.8	12.6	3.5	1,560
String Bean (green).....	2.3	7.4	0.3	89.2	0.8	190
Apple (edible portion)...	0.4	14.2	0.5	84.6	0.3	285
Corn.....	10.0	73.4	4.3	10.8	1.5	1,685
Rice.....	8.0	77.0	2.0	12.0	1.0	1,620
Peanut.....	25.8	24.4	38.6	9.2	2.0	2,485

780. **Digestion.** — When food is taken into the body it comes in contact with certain digestive ferments or enzymes secreted in different parts of the alimentary canal. These enzymes have not been prepared in a state of purity, and their chemical nature is not fully known.

One of the first enzymes with which our food comes in contact is *ptyalin*, which is present in saliva. Ptyalin converts starch, first into soluble starch and finally into glucose. The enzyme maltase is also present in saliva.

Pepsin is a very important enzyme present in the gastric juice. It is the agent by which albuminous matter or proteins, such as lean meat and eggs, are converted into soluble peptones, in the stomach, and thus rendered fit for absorption. Normally, there is about 0.2 per cent, or a little more, of HCl in the gastric juice of man. By the action of this acid the proteins are first converted into syntonin, which is then transformed by pepsin into peptones.

Lipase, another enzyme in the gastric juice, hydrolyzes emulsified fat (*e.g.*, in milk) into acid and glycerine.

The pancreatic juice of the small intestine furnishes *trypsin*, which converts the remaining proteins into peptones or amino-acids. These pass through the walls of the intestine into the circulation.

The *steapsin* (pancreatic lipase) of the intestinal juice also hydrolyzes fat (in the intestine) to glycerine and acids, which then diffuse through the intestinal wall to recombine, forming fat in the blood. In case of jaundice, bile is prevented from reaching the intestine, so the utilization of fat is strikingly diminished.

Amylopsin, a starch-splitting enzyme of the pancreatic juice, also plays an important rôle in digestion.

Some of the substances obtained by the digestion of food are utilized in growth and repair, some are stored as fat, and some

are oxidized to produce power and heat. The waste products of the body, such as carbon dioxide, water, and urea, are excreted.

EXERCISES

1. Compare the synthetic power of plants and of animals.
2. What chemical elements may be regarded as essential ones in green plants and in animals?
3. Explain, and also illustrate, the term photosynthesis.
4. How did Baly synthesize sugars?
5. How could you prove that plants absorb carbon dioxide in sunlight and give it off in darkness?
6. How did Liebig discover the connection between soil and crops?
7. Discuss in a broad way the fertilization of crops.
8. Explain the following: (1) "superphosphate of lime"; (2) symbiotic bacteria; (3) hydrolysis of urea; (4) indirect fertilization; and (5) the conversion of ammonia (in the soil) into nitrates.
9. What rôle do soil bacteria play?
10. What is meant by the irradiation of food materials?
11. Enumerate the constituents of the food of man and point out the rôle of each.
12. Give an account of the vitamins. Where do they occur?
13. Select a diet suitable for the "average man" doing a moderate amount of work; also for a man of sedentary occupation. Estimate, according to current market prices, the cost per day to supply the food.
14. Name some important digestive ferments (enzymes) and show what part they play in digestion.

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PROBLEMS

PERCENTAGE COMPOSITION

1. Calculate the percentage composition of lead nitrate, calcium phosphate, limonite ($2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$), Paris green ($\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{Cu}_3(\text{AsO}_3)_2$) and calcium bicarbonate ($\text{Ca}(\text{HCO}_3)_2$).
2. Calculate the percentage composition of ordinary alum ($\text{K}_2\text{Al}_2(\text{SO}_4)_4 \cdot 24\text{H}_2\text{O}$) and of potassium ferrocyanide ($\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$).
3. Calculate the percentage composition of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$).
4. Calculate the percentage of water in crystallized copper sulfate or blue vitriol ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$).
5. Calculate the percentage of copper in the mineral azurite ($\text{Cu}(\text{OH})_2 \cdot 2\text{CuCO}_3$). Ans. 55.34 per cent.
6. Find the percentage of silver in $\text{NaAg}(\text{CN})_2$ and of uranium and vanadium in carnotite ($\text{K}_2\text{O} \cdot 2\text{UO}_3 \cdot \text{V}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$).
7. Find the percentage of copper in the mineral enargite ($3\text{Cu}_2\text{S} \cdot \text{As}_2\text{S}_5$).
8. Find the percentage of SiO_2 in talc ($\text{Mg}_3\text{H}_2(\text{SiO}_3)_4$) and of Al_2O_3 in kaolinite ($\text{Al}_2\text{H}_2(\text{SiO}_4)_2 \cdot \text{H}_2\text{O}$).
9. Find the percentage composition of feldspar (KAlSi_3O_8) expressed as K_2O , Al_2O_3 , and SiO_2 .
10. Calculate the percentage of phosphorus in apatite ($\text{Ca}_4(\text{CaF})(\text{PO}_4)_3$).

FORMULAE AND EQUIVALENT WEIGHTS

11. A specimen of the mineral chalcopyrite yielded on analysis 34.40 per cent of copper, 30.47 per cent of iron, and 35.87 per cent of sulfur. Derive its empirical formula.
12. 2.6 g. of mercurous oxide were heated, and yielded 0.1 g. of oxygen. Find the simplest formula of the compound and the equivalent weight of mercury in this oxide.
13. A compound on analysis yielded 22.77 per cent of sodium, 21.78 per cent of boron, and 55.45 per cent of oxygen. Calculate its simplest formula.
14. 2.238 g. of pure iron combined with oxygen to form 3.198 g. of dried rust. Find the equivalent weight of iron and the simplest formula for this oxide of iron.
15. A compound contains 26.53 per cent of potassium, 35.37 of chromium, and 38.10 of oxygen. Find its simplest formula.
16. Derive the empirical formula of mercuric cyanide, 10.8 g. of which lost 2.2 g. of cyanogen upon heating.
17. Find the formula of the hydrate aluminium sulfate, 4.77 g. of which lost 2.305 g. of water when heated to constant weight.
18. Analysis shows that a certain compound contains the following percentages: calcium oxide, 1.90; alumina, 37.72; silica, 23.53; water, 36.85. Find its empirical formula.

19. 3.167 g. of aluminium hydroxide lost 1.0933 g. of water when heated to constant weight. Find its simplest formula.

20. A silicate of calcium and magnesium contains the following percentages: calcium, 8.32; magnesium, 15.16; silicon, 23.29; oxygen, 53.23. Find its simplest formula.

21. Find the simplest formula of the substance having the following composition: K, 8.24; Al, 5.69; S, 13.50; O, 27.01; H_2O , 45.56.

22. Assign a formula to the substance which, by analysis, yielded the following percentage composition: Al_2O_3 , 16.86; CaO , 9.20; SiO_2 , 59.28; H_2O , 14.66.

23. Three oxides of nitrogen contain, respectively, the following percentages of nitrogen: 63.65, 46.68, and 36.86. Find the equivalent of nitrogen in each compound.

24. 1.665 g. of lead chloride yielded 1.778 g. of silver chloride. What is the equivalent of lead?

25. If 2.1765 g. potassium bromide required, for complete precipitation, 1.993 g. of pure silver dissolved in nitric acid, what is the equivalent of bromine?

THE EFFECT OF PRESSURE AND TEMPERATURE UPON GASES

How does the density of a gas vary with the pressure when the temperature is constant? Write down a statement of Boyle's law and express it mathematically. A liter of hydrogen at 0°C . and 760 mm. weighs .08987 g.

What vol. in liters will this wt. of H_2 occupy at 0°C . and $1/8$ an atm.?

"	"	"	"	"	"	$1/2$	"
"	"	"	"	"	"	$3/4$	"
"	"	"	"	"	"	$1\ 1/2$	"
"	"	"	"	"	"	2	"
"	"	"	"	"	"	4	"

Procure a piece of coördinate paper and plot these points — pressures as ordinates and volumes as abscissae — and connect the points with a curve which will be the graph of the volume of .08987 g. of hydrogen at 0°C . From this graph determine the volume when the pressure is 0.8 atm.; 3 atm.

A gas, as a rule, is not measured at the desired pressure, but from the above statements it will be seen that we may find out what the volume is at any desired pressure, either from a graph or, more simply, by calculation.

26. 25 cc. of hydrogen were collected under a pressure of 720 mm. What is its volume at 760 mm.?

27. 42 cc. of gas were collected under a pressure of 800 mm. What is the volume at 760 mm.?

28. 100 cc. of hydrogen at 760 mm. are compressed until its volume is 85 cc. What is the new pressure?

How does the volume of a gas vary with the temperature when the pressure is constant? Write a statement of Charles' law and express it mathematically.

At 760 mm. and 0°C . 0.08987 g. of hydrogen occupy 1,000 cc.

What volume will this weight of gas occupy at 760 mm. and 50° ?

"	"	"	"	"	100°
"	"	"	"	"	-50°
"	"	"	"	"	-100°

Plot these points on coördinate paper, using the volumes for ordinates and the temperatures for abscissae. Connect these points by a line which is to be extended until it cuts the abscissa.

What are the fixed points in thermometry? What is the absolute zero? How do we obtain the absolute temperature (T) from the centigrade temperature (t)? Does the plotted curve show that the volume of a gas is proportional to the absolute temperature?

29. 10.5 cc. of a gas at 21° C. will occupy what volume at 0° C.?

30. 30 cc. of oxygen are at 16° C. What would the volume be at 55° F.?
Ans. 29.67 cc.

31. 25 cc. of a gas were collected at 20° C. and under a pressure of 750 mm. What is the volume under standard conditions? *Ans.* 22.99 cc.

32. 23.4 cc. of air are measured at -10° F. and 730 mm. What will the volume be at 0° C. and 760 mm.? *Ans.* 24.58 cc.

33. 34.6 cc. of hydrogen are collected at 17° C. and under pressure of 780 mm. What is the volume at 75° F. and 750 mm.? *Ans.* 36.84 cc.

34. How many grams of potassium chlorate are required to prepare a liter of oxygen at 22° C. with the barometer at 765 mm. *Ans.* 3.398 g.

35. The result of a calculation gave 22.4 cc. of a gas at 0° C. and 760 mm. The gas was collected at 20° C. and 770 mm. What was the observed volume, and what was the weight of the gas, if a liter of it, at standard conditions, weighs 1.430 g.? *Ans.* 23.73 cc.
0.03203 g.

36. Suppose we have 250 cc. of nitrogen at 60° F. and 730 mm. pressure, what will the volume be if the temperature becomes 30° C. and the pressure 780 mm.? *Ans.* 245.6 cc.

37. Reduce 60 cc. of oxygen, measured over water at 20° C. and 763 mm. to the *dry* condition and to 0° C. and 760 mm.

38. The result of a calculation gave 3.55 liters of hydrogen at S.T.P. The gas was collected over water at 18° and under a pressure of 763 mm. What was the observed volume? *Ans.* 3.85 liters.

39. 100 cc. of hydrogen at 20° and 756 mm. will have what volume at -10° and 761 mm.? *Ans.* 89.16 cc.

40. The result of a calculation gave 22,400 cc. of a pure, dry gas at 0° and 760 mm. The gas was collected over water at 25° and 755 mm. Find the observed volume of the gas and the weight, if a liter of the dry gas at 0° and 760 mm. weighs 1.251 g. *Ans.* 25,405 cc.
28.022 g.

41. One liter of oxygen, at S.T.P., weighs 1.429 g. 350 cc. of this gas measured over water at 22° and 753 mm. will contain what weight of the dry gas? *Ans.* 0.4467 g.

42. What is the absolute density of air at 21° and 762 mm.? of hydrogen at -10° and 745 mm.? *Ans.* Density of air = 0.001204.
Density of hydrogen = 0.0000916.

43. The density of a substance referred to air is 2.21. What is its density referred to oxygen and to hydrogen, and what volume would 2 g. of the substance occupy at 21° and 765 mm.? *Ans.* Density referred to oxygen = 1.999.
Density referred to hydrogen = 31.82.
Volume = 750.2 cc.

44. Reduce 60 cc. of gas at 21° C. and 740 mm. to 21° F. and 755 mm.

Ans. 55.85 cc.

45. A flask while open to the air is heated to $100^{\circ}\text{C}.$, the barometric pressure being 766 mm. It is then closed and allowed to cool to $22^{\circ}\text{C}.$ Find the final pressure.

Ans. 605.8 mm.

46. A quantity of oxygen has a volume of 40 cc. at $27^{\circ}\text{C}.$ At what temperature would its volume become 30 cc.?

Ans. $-48^{\circ}\text{C}.$

47. A quantity of air having a volume of 125 cc. and a pressure of 755 mm. is expanded, the temperature being kept constant, to a volume of 625 cc. Find the final pressure.

Ans. 151 mm.

48. A flask is filled with air at $-10^{\circ}\text{F}.$ and 755 mm. If the barometric pressure remains constant, to what temperature must the flask be raised to drive out half of the air that was in it when it was filled?

Ans. $226.3^{\circ}\text{C}.$

49. A volume of nitrogen in a tube over mercury measured 60 cc. The mercury in the tube was 50 mm. above the surface of the mercury in the trough, and the barometric pressure was 755 mm. What would have been the volume if exposed to the standard pressure alone? What would be the volume of nitrogen if the tube were forced down until the mercury in the tube is 50 mm. below the surface of the mercury in the trough?

Ans. 55.66 cc.

52.54 cc.

50. One liter of oxygen, at S.T.P., weighs 1.429 g. What weight of the gas is contained at $20^{\circ}\text{C}.$ in a tank having a capacity of 2.5 liters, the pressure being 10 atmospheres?

Ans. 33.29 g.

51. The density of a certain gas is .001204 at $21^{\circ}\text{C}.$ and 762 mm. Find the weight of a liter of the gas at S.T.P.

52. A glass bottle is capable of standing a pressure of 5 atmospheres. If the bottle be filled with oxygen at $-10^{\circ}\text{C}.$ and 760 mm., to what temperature should the gas be heated to burst the bottle?

WEIGHT AND VOLUME

53. What volume of oxygen, measured at 20° and 745 mm., can be obtained by strongly heating 7 g. of potassium chlorate?

54. How many grams of each of the following substances would have to be heated to obtain 3 liters of oxygen: (a) Mercuric oxide, (b) manganese dioxide, (c) barium peroxide?

Ans. (a) 58.01 g. $\text{HgO}.$

(b) 34.93 g. $\text{MnO}_2.$

(c) 45.37 g. $\text{BaO}_2.$

55. What volume of chlorine gas could be obtained from 200 g. of sodium chloride? What volume of hydrogen chloride could be obtained by allowing this volume of chlorine to unite with hydrogen?

Ans. 38.32 liters of chlorine.

56. A quantity of carbon monoxide was passed through a red-hot tube containing ferric oxide. The resulting gas was absorbed by caustic potash, the gain in weight being 1 g. What volume of carbon monoxide at S.T.P. was required?

Ans. 0.507 liter.

57. A certain weight of potassium chlorate was heated until completely decomposed, and the residue weighed 24.62 g. What weight of potassium chlorate was heated, and what weight of oxygen was obtained?

Ans. 40.47 g. $\text{KClO}_3.$

15.85 g. $\text{O}_2.$

58. How many grams of sulfuric acid containing 16 per cent of H_2SO_4 will it take to dissolve 100 g. of zinc?

Ans. 936.5 g.

59. How many grams of hydrogen will be liberated when 40 g. of zinc alloy containing 10 per cent of magnesium are dissolved by hydrochloric acid? How many grams of acid will be used up, and how much zinc and magnesium chloride will be formed?

Ans. 1.43 g. H_2 .
52.17 g. HCl .
75.08 g. $ZnCl_2$.
15.68 g. $MgCl_2$.

60. What weight of sulfuric acid containing 12 per cent of H_2SO_4 will dissolve 5 g. of iron wire 99.6 per cent pure?

Ans. 72.89 g.

61. How many kilograms of sodium chloride are necessary to prepare 60 kilograms of hydrochloric acid containing 25 per cent of available acid?

Ans. 24.04 kg.

62. What weight of magnesium would be required to generate hydrogen enough to fill a balloon with a capacity of 20 liters, at 22° and 775 mm.?

Ans. 20.48 g.

63. What volume of hydrogen measured over water at 21° and 750 mm. will be liberated when 20 g. of an alloy containing 90 per cent of zinc and 10 per cent of magnesium are dissolved in hydrochloric acid?

64. How much chlorine by weight and by volume (S.T.P.) can be obtained from 75 g. of pure salt? What volume would the gas occupy at 10° and 735 mm.?

Ans. 45.52 g.
14.36 liters.
15.39 liters.

65. How many grams of iron are required completely to reduce 10 liters of water vapor measured at 130° and 745 mm.?

Ans. 12.41 g.

66. If the density of sulfur dioxide under certain conditions is 0.003, what volume of the gas would be produced, under these conditions, by burning 12 g. of sulfur?

67. (a) What volume of nitrogen at 20° and 770 mm. can be obtained by heating 33 g. of ammonium nitrite? (b) What volume would the gas occupy at $65^\circ F.$ and 745 mm.?

Ans. (a) 12.23 liters.
(b) 12.57 liters.

68. How large a tank could be filled with acetylene gas, at 21° and 765 mm., by decomposing 100 kilograms of calcium carbide with water?

Ans. 37,450 liters.

69. The formula of gypsum is $CaSO_4 \cdot 2H_2O$. What volume of water vapor, at $300^\circ C.$ and 750 mm., would be liberated by heating 172 g. of gypsum?

Ans. 95.28 liters.

70. A specimen of iron pyrites was found on analysis to contain 50 per cent of sulfur. Suppose that all the sulfur in 5 kilos. of the mineral is oxidized to sulfur dioxide, what are the weights and volumes of the gases at 25° and 110 mm.?

Ans. 5 kg. SO_2 and 2.5 kg. O_2 .
13,200 liters.

71. Ten grams of an alloy of zinc and magnesium (containing 10 per cent Mg .) were placed in a flask containing 90 g. of sulfuric acid (25 per cent H_2SO_4). What weight and volume of hydrogen were liberated?

Ans. 0.3575 g.
3.977 liters.

72. How many cubic centimeters of carbon dioxide, measured at 20° and 745 mm., will be absorbed by a solution containing 3 g. of sodium hydroxide, to form sodium carbonate?

Ans. 919.4 cc.

73. A sample of Epsom salt ($MgSO_4 \cdot 7H_2O$), after heating until it became

anhydrous, left a residue weighing 4 g. Find the weight of the original sample, and the volume which the water would occupy at S.T.P.

74. What volume of hydrogen sulfide (S.T.P.) is needed to reduce 2.4 g. of potassium permanganate in sulfuric acid solution?

75. What volume of methane, measured over water at 20° and 765 mm., could be obtained by heating 5.25 g. of anhydrous sodium acetate with excess of soda-lime? What volume of pure oxygen (S.T.P.) would be required completely to burn the methane?

76. Assuming that the temperature and pressure are constant, what volume of gaseous product may be obtained by exploding a mixture of 125 cc. of carbon monoxide and 60 cc. of oxygen?

77. A mixture of 150 cc. of methane and 75 cc. of oxygen was exploded by means of an electric spark. Find the volume of the product after the removal of aqueous vapor by absorption in phosphoric anhydride, assuming that the temperature is 100° C. and the pressure 760 mm. throughout.

78. 100 cc. of a mixture of nitrogen and methane were exploded with 200 cc. of oxygen. The volume of the *dry* gaseous product was found to be 250 cc. Find the percentage of methane in the original sample, assuming that the pressure and temperature are constant throughout.

Ans. 25 per cent.

79. If a paraffin candle (C 85 per cent, H 15 per cent) loses 40 g. by burning, find the weights and volumes of the products of combustion and of the oxygen used, assuming that the pressure is 770 mm. and the temperature 102° .

Ans. 54 g. and 91.1 liters H_2O ,
124.67 g. and 86 liters CO_2 ,
138.67 g. and 131.5 liters O_2 .

80. Sodium peroxide, when added to water, liberates 3.5 liters of oxygen when collected over water at 21° and 763 mm. Find the weight of peroxide decomposed and the weight of sodium hydroxide formed.

Ans. 22.18 g. Na_2O_2 ,
22.75 g. NaOH .

81. A sample of water glass weighing 1.189 g. yielded upon analysis 0.072 g. of SiO_2 and 0.2307 g. of a mixture of NaCl and KCl . From the mixed chlorides 0.0687 g. of K_2PtCl_6 was obtained. Calculate the percentages of Na_2O , K_2O , and SiO_2 contained in the sample analyzed.

Ans. 6.06 per cent SiO_2 ,
9.38 per cent Na_2O ,
1.12 per cent K_2O .

82. If 1 g. of water at 20° absorbs 0.526 g. of ammonia gas, how much ammonium sulfate would be required to prepare enough of the gas to saturate 1,000 g. of water at 20° ? What volume would the gas occupy if measured dry at 22° and 745 mm.?

83. (a) What weight of quartz sand should be necessary to flux the lime contained in 1 kilogram of limestone containing 85 per cent of calcium carbonate?

(b) What volume of carbon dioxide, measured at 25° and 765 mm., should be produced?

84. A dilute solution of sulfuric acid was electrolyzed and the evolved gases collected above the electrodes. What were the volumes occupied by the moist hydrogen and oxygen when 0.03 g. of water had been decomposed, the temperature being 23° and the pressure 775 mm.?

MOLECULAR FORMULAE, MOLECULAR WEIGHTS, AND ATOMIC WEIGHTS

85. A compound contains 17.647 per cent of hydrogen and 82.353 per cent of nitrogen, and its specific gravity (air = 1) is 0.5886. What is the formula of the compound?

86. A compound contains 85.71 per cent of carbon and 14.29 per cent of hydrogen, and its sp. gr. (air = 1) is 0.97. What is its formula?

87. The weight of 1 liter of gas at 0° and 760 mm. is 5.236 g. What is its density referred to air and to hydrogen, and what is its molecular weight?

88. The weight of 1 liter of gas at 0° and 760 mm. is 1.628. What is the molecular weight of the gas?

89. 111.4 cc. of a gas at 27° and 750 mm. weigh 0.1537 g. What is its molecular weight?

90. If the vapor density of phosphorus is 4.3 (air = 1) and its atomic weight 31, what is its molecular weight? What is its molecular formula?

91. The specific gravity of sulfur dioxide (oxygen = 1) is 2.002. What is its molecular weight?

92. 8.019 cc. of a gas collected at 20° and 742.4 mm. pressure weighed 14 g. What is its molecular weight? *Ans.* 42.96.

93. From the following data find the atomic weight of chlorine and assign formulae to the compounds. (Atomic weights: O = 16, C = 12, H = 1.008, P = 31.)

Compounds	Weight 22.4 L	Weight Hydrogen	Weight Chlorine	Weight Carbon	Weight Oxygen	Weight Phosphorus
Hydrogen chloride...	36.468	1.008	35.46
Phosgene.....	98.92	..	70.92	12	16	..
Phosphorus trichlo- ride.....	137.38	..	106.38	31
Phosphorus oxychlo- ride.....	153.38	..	106.38	..	16	31
Chlorine dioxide.....	67.46	..	35.46	..	32	..
Chloroform.....	119.388	1.008	106.38	12
Carbon tetrachloride	153.84	..	141.84	12

94. The weight of 1 liter, at S.T.P., of each of several elementary substances is as follows:

Hydrogen.....	0.08987 g.
Oxygen.....	1.429 "
Nitrogen.....	1.2507 "
Chlorine.....	3.22 "
Mercury (vapor).....	8.87 "
Ozone.....	2.14 "

Find the molecular weight and select the molecular formula of each substance.

95. If the specific heat of zinc is 0.094 and the equivalent weight is 32.7, what is its exact atomic weight?

96. Platinic chloride contains 57.92 per cent of platinum and 42.08 per cent of chlorine. The specific heat of platinum is 0.0324; calculate (a) the exact atomic weight of platinum and (b) the formula of platinic chloride.

97. 44.5274 g. of NaCl were dissolved in water and treated with silver nitrate. The pure silver chloride obtained weighed 109.1897 g. Taking the atomic weight of silver as 107.88 and that of chlorine as 35.46, find the atomic weight of sodium.

98. Derive the formula of the hydrate Glauber's salt, 8.16 g. of which lost 4.51 g. of water upon heating.

99. 2.3737 g. of gypsum were heated to constant weight, which was found to be 1.8768 g. Find the formula of gypsum, assuming the formula of calcium sulfate to be CaSO_4 .

100. Assign a formula to the substance which, by analysis, yielded the following percentage composition: Al_2O_3 , 16.86, CaO , 9.20, SiO_2 , 59.28, H_2O , 14.66.

101. According to Stas, 53.1958 g. of silver form 92.6042 g. of silver bromide. Calculate the atomic weight of silver, given the atomic weight of bromine as 79.92.

102. A carbon compound by analysis yielded the following percentages: C 30.45, H 3.83, Cl 45.69, O 20.23. The specific gravity of its vapor referred to air was found to be 5.48. Find the formula of the compound.

103. The freezing point of a 3.3 per cent solution of hydrogen peroxide in water was found to be -2.03°C . Calculate the depression produced by 3.3 g. of hydrogen peroxide in 1,000 g. of water, and from the value thus obtained find out the weight of hydrogen peroxide required to produce a depression of 1.86°C . in 1,000 g. of water, and then assign the formula to the compound?
Ans. -0.196°C .

31.3.

104. If 5 g. of a substance, dissolved in 1,000 g. of water, gave a solution freezing at -0.2°C ., what is the molecular weight of the substance?

Ans. 47.

105. A clean, dry flask full of air was tightly stoppered at 26° and 753 mm. and its weight was found to be 44.051 g. The flask was then filled with pure carbon dioxide under the same conditions, the weight of the stoppered flask and carbon dioxide being 44.2212 g. Finally, the carbon dioxide was removed from the flask, the vessel filled up to the cork with distilled water, and the weight found to be 319 g. Calculate the molar weight of carbon dioxide, *i.e.*, the weight of 22.4 liters at S.T.P.

NOTE.—Let x = wt. of the flask; then $(44.051 - x)$ = wt. of air, and $(44.2212 - x)$ = wt. of carbon dioxide. $319 - x$ = vol. of flask = vol. of gas. It follows from this that $x = 43.733$ g., and the volume of the flask is 275.3 cc., which is 249.1 cc. at S.T.P. The molar weight of CO_2 may now be calculated.

Ans. 43.9.

106. According to experiments of Marignac, 5 g. of strontium chloride, containing 6 molecules of water of hydration, yielded 3.442 g. of strontium sulfate. Find the equivalent weight of strontium.

107. A liter of oxygen weighs 1.429 g. A liter of the gas of a certain gaseous element, the molecules of which are diatomic, weighs 1.2507 g. Find the atomic weight of the element.

108. The analysis of a compound containing carbon, hydrogen, nitrogen, and oxygen yielded the following results: 0.2169 g. of the substance, when oxidized, gave 0.517 g. of CO_2 and 0.0685 g. of H_2O . 0.2218 g. of the compound, when decomposed, gave 17.4 cc. of nitrogen, measured over water at 6°C ., and 762 mm. First find the percentage composition of the compound and then its simplest formula.

NORMAL SOLUTIONS AND EQUIVALENT WEIGHTS

109. Calculate the number of grams of each of the most important bases and acids required to prepare a liter of a normal solution; also a liter of a molar solution.

110. (a) 20 cc. of normal sulfuric acid are used to neutralize a solution of sodium carbonate. How many equivalents of sodium carbonate were in the solution? How many grams of sodium carbonate?

(b) Repeat the problem using sodium hydrogen carbonate in place of sodium carbonate.

111. How many equivalents of chlorine are precipitated by 20 cc. of a normal solution of silver nitrate? How many grams of silver and of chlorine are present in the precipitate?

112. If the bromine in 15 g. of potassium bromide be liberated in 5.5 liters of solution, find the concentration of the solution in equivalents and in grams.

Ans. 0.023 equiv.

1.833 g. of bromine per liter.

113. If 35.5 cc. of normal potassium hydroxide are required to neutralize 25 cc. of sulfuric acid, what is the normality of the acid?

114. What volume of $N/5$ hydrochloric acid would be required to decompose 120 cc. of $N/2$ sodium bicarbonate?

115. (a) What volume of normal sulfuric acid can be neutralized by 15 g. of washing soda ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$)?

(b) One gram of baking soda, dissolved in water, required 10 cc. of normal acid to neutralize it. What per cent of sodium bicarbonate did the soda contain?

Ans. (a) 104.9 cc. acid.

(b) 84 per cent of NaHCO_3 .

116. What weight of chlorine is present per cc. of $N/10$ calcium chloride solution? What weight of silver nitrate would be required to combine with the chloride present in 16 cc. of the solution? *Ans.* 0.00355 g. of chlorine.

0.272 g. of AgNO_3 .

117. How many cc. of $N/10$ chlorine water must be added to a solution containing 1.3 g. of potassium iodide in order to set free all the iodine?

Ans. 78.3 cc.

118. An excess of ferrous sulfide was added to 80 cc. of a dilute sulfuric acid and the volume of H_2S set free measured 650 cc. at S.T.P. Calculate the normality of the acid.

Ans. 0.725 N .

119. What volume of hydrogen at S.T.P. should be obtained by treating 35 cc. of $N/2$ sulfuric acid with an excess of magnesium? *Ans.* 196 cc.

120. If 9.8 g. of phosphoric acid are present in 1 liter of a solution, what is (1) the normal concentration and (2) the molar concentration?

121. If 22 g. of strontium hydroxide are present in 6.5 liters of a solution, what is (1) the normal concentration and (2) the molar concentration?

Ans. (1) 0.0556 N .

122. How many equivalents of a base can be neutralized by 22 cc. of $N/5$ acid? How many grams of base were present if the base was (1) sodium hydroxide, (2) calcium hydroxide?

Ans. 0.0044 equiv.

0.176 g. NaOH .

0.1628 g. $\text{Ca}(\text{OH})_2$.

123. If 10 cc. of a certain sulfuric acid solution yield 0.1220 g. of barium sulphate, how much must the solution be diluted for an exactly $N/10$ solution?

Ans. 10 cc. to 10.45 cc.

124. 1.831 g. of zinc were dissolved in an excess of hydrochloric acid, the hydrogen collected over water, and the volume found to be 715 cc. at a temperature of 23° and a pressure of 758 mm. Find the volume of hydrogen, at S.T.P., and the equivalent weight and valence of zinc.

Ans. 639.6 cc. hydrogen.

32.11, the equiv. wt.

125. 50 cc. of dilute hydrochloric were required to decompose 2.3 g. of baking soda, and the volume of gas formed occupied 500 cc. at S.T.P. Find the normality of the acid and the percentage of sodium bicarbonate in the baking soda.

Ans. 0.446 *N*.

81.5 per cent NaHCO_3 .

126. 18.50 cc. of a decinormal solution of iodine were required in the titration of 25 cc. of a solution of sodium arsenite (Na_3AsO_3). What was the normality of the arsenite solution? How many grams of arsenic were present in the sample?

127. Ten cc. of a liquid brass polish containing oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) required 22.5 cc. of normal sodium hydroxide solution to neutralize it. What weight of oxalic acid did the sample contain?

128. Calculate the equivalent weights of the following oxidizing or reducing agents: potassium dichromate, potassium permanganate in alkaline solution, iodine, Mohr's salt ($\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$).

129. 0.2815 g. of calcium carbonate was dissolved in 30 cc. of normal hydrochloric acid and the excess of acid determined by normal sodium hydroxide, of which 24.43 cc. were required. What percentage of carbon dioxide did the sample contain?

Ans. 43.52 per cent.

130. 0.25 g. of impure pyrolusite was treated with hydrochloric acid and the chlorine passed into an excess of potassium iodide solution. The liberated iodine required for decolorization 50 cc. of a solution of arsenious acid that had been made equivalent to $N/10$ iodine solution. What per cent of manganese dioxide did the pyrolusite contain?

Ans. 86.9 per cent.

131. A slight excess of barium chloride solution was added to 240 cc. of dilute sulfuric acid, and the barium sulfate precipitated weighed 3.85 g. Calculate the normality of the acid.

Ans. 0.1375 *N*.

132. 1.156 g. of a solution containing caustic potash was diluted with water and titrated with $N/10$ H_2SO_4 , of which 36.4 cc. were required. Calculate the percentage of KOH in the sample taken for analysis.

Ans. 17.64 per cent.

133. An excess of potassium bicarbonate was added to 125 cc. of dilute sulfuric acid and the volume of gas liberated, measured dry at 20° and 765 mm., was 2.5 liters. Find the normality of the acid.

134. What weight of Mohr's salt would be required to reduce 60 cc. of $N/10$ potassium permanganate?

135. 12.5 cc. of $N/5$ hydrochloric acid would decompose what weight of limestone containing 90 per cent of calcium carbonate? Find the weight of gas liberated.

136. What volume of nitric oxide, measured over water at 21° and 758 mm., could be obtained by the action of 25 cc. of 7 *N* nitric acid upon pure copper?

137. 0.521 g. of Mohr's salt is dissolved in pure water, acidified with sulfuric acid, and then oxidized by $N/10$ potassium permanganate. What volume of the solution is required, and what weight of permanganate does it contain?

138. A mixture of 2.1 g. of sodium bicarbonate and silica was treated with

50 cc. of dilute hydrochloric acid and the gas formed had a volume of 400 cc. (S.T.P.). Find the percentage of sodium bicarbonate in the mixture and the normality of the acid.

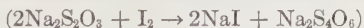
139. How many grams of arsenious oxide are required to prepare a liter of normal arsenious acid for (1) oxidation-reduction reactions, and (2) for neutralization reactions?

140. 10.09 g. of magnesium nitride are heated with excess of water, the ammonia evolved is dissolved in water, and the solution diluted to 500 cc. Find the normality of the solution, and the volume of $N/10$ sulfuric acid required to neutralize 10 cc. of this solution.

141. Determine the normality of a potassium dichromate solution, 25 cc. of which oxidized, in acid solution, 1 g. of ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) to ferric salt.

142. One gram of a mixture of pure potassium chloride and pure sodium chloride was dissolved in about 100 cc. of water, a few drops of neutral potassium chromate were added, and the chlorine was determined by titration with an exactly $N/10$ solution (neutral) of silver nitrate. 141 cc. were necessary to give the faint red tint. Find the amount of chlorine present, and then calculate the amounts of potassium chloride and sodium chloride in the mixture.

143. Determine the purity of a sample of pyrolusite, 2.2 g. of which, with excess of hydrochloric acid, liberated sufficient chlorine to set free a quantity of iodine that required 250 cc. of $N/5$ sodium thiosulfate for titration.



144. (a) What volume of carbon dioxide, measured dry at 20° and 750 mm., should be absorbed by a solution containing 4 g. of sodium hydroxide, assuming that sodium carbonate is formed?

(b) What volume of $N/5$ acetic acid would be required to decompose the salt?

APPENDIX

I. LOGARITHMS

No.	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4	8	12	17	21	25	29	33	37
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30	34
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	10	14	17	21	24	28	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21	24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6386	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7
	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9

APPENDIX

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LOGARITHMS — *Continued*

No.	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7992	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	1	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	1	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9594	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4
	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9

II. WEIGHTS AND MEASURES

METRIC SYSTEM

Measures of Length

<i>Meter</i>		<i>Decimeters</i>		<i>Centimeters</i>		<i>Millimeters</i>		<i>Inches</i>
1	=	10	=	100	=	1000	=	39.37100
		1	=	10	=	100	=	3.93710
				1	=	10	=	0.39371
						1	=	0.03937

Measures of Capacity

<i>Liter</i>		<i>Cubic Centimeters</i>		<i>Pints</i>		<i>Cubic inches</i>
1	=	1000	=	2.113 (U.S.)	=	61.0363
		1	=	0.002113 (U.S.)	=	0.0610
		16.38			=	1.00

Measures of Weight

<i>Kilogram</i>		<i>Grams</i>		<i>Lbs. (Avoirdupois)</i>		<i>Grains</i>
1	=	1000	=	2.2046	=	15432.00
		1	=	0.0022	=	15.43
Linear	{	10 millimeters (mm)			=	1 centimeter (cm).
		10 centimeters			=	1 decimeter (dm).
		10 decimeters			=	1 meter (m).
		Equivalent. 1 inch			=	2.54 cm (nearly).
Cubic	{	1000 cubic millimeters			=	1 cubic centimeter (cc).
		1000 cubic centimeters			=	1 cubic decimeter (cdm).
		1000 cubic decimeters			=	1 cubic meter (cbm).
		Equivalents } 1000 cc			=	1 liter (l).
Weight	{	1l			=	1 quart (nearly).
		10 milligrams (mg)			=	1 centigram (cg).
		10 centigrams			=	1 decigram (dg).
		10 decigrams			=	1 gram (g).
		1000 grams			=	1 kilogram (k).
		1cc of water (at 4° C.)			=	1g.
		1l of water (at 4° c.)			=	1k.
Conversion. {	{	28.3g = 1 oz. (nearly)				
		1k = 2½ lb. (nearly).				
		1g = 15 gr. (nearly).				
		1000k = 2205 lbs.			=	1 metric ton.
		1 lb. avoird. = 453.6 g.				

III. CORRECTIONS FOR READING OF THE BAROMETER FROM 15° C. TO 30° C., AND AT 750 MM.

The column of mercury expands with rising temperature, consequently a correction must be made in order to reduce the column of mercury to 0° C.

Temperature	Correction for Barometer with Glass Scale.	Correction for Barometer with Brass Scale.
15°	2. mm.	1.8 mm.
16	2.1	2.0
17	2.2	2.1
18	2.3	2.2
19	2.5	2.3
20	2.6	2.5
21	2.7	2.6
22	2.8	2.7
23	3.0	2.8
24	3.1	2.9
25	3.2	3.1
26	3.4	3.2
27	3.5	3.3
28	3.6	3.4
29	3.7	3.6
30	3.9	3.7

IV. VAPOR PRESSURES OF WATER EXPRESSED IN MILLIMETERS OF MERCURY

0°	4.6	26°	25.0
5°	6.5	27°	26.5
10°	9.1	28°	28.1
11°	9.8	29°	29.7
12°	10.4	30°	31.5
13°	11.1	40°	54.9
14°	11.9	50°	92.0
15°	12.7	60°	148.9
16°	13.5	70°	233.3
17°	14.4	80°	354.9
18°	15.3	90°	525.5
19°	16.3	97°	681.9
20°	17.4	100°	760.0
21°	18.5	120°	1491.3
22°	19.6	150°	3581.2
23°	20.9	180°	7546.4
24°	22.2	220°	17390.4
25°	23.7		

V. ABSOLUTE DENSITY OF WATER (DENSITY IN GRAMS PER CUBIC CENTIMETER)

0°	0.999841	10°	0.999700
1°	0.999900	15°	0.999099
2°	0.999941	20°	0.998203
3°	0.999965	25°	0.997044
4°	0.999973	30°	0.995646
5°	0.999965		

VI. DENSITIES, MELTING POINTS, AND BOILING POINTS OF SOME OF THE METALS

Metal	Density (Mass of 1 cc.)	Melting Point °C.	Boiling Point °C.
Aluminium	2.7	659	1800
Antimony.....	6.7	630	1380
Arsenic.....	5.7	814 (36 atm.)	615
Barium.....	3.5	850	1140
Beryllium.....	1.84	1350	1500
Bismuth.....	9.8	271	1450
Cadmium.....	8.6	321	785
Calcium.....	1.55	810	1170
Cerium.....	6.9	640	1400
Chromium.....	7.1	1615	2200
Cobalt.....	8.9	1480	2900
Copper.....	8.93	1083	2300
Gold.....	19.3	1063	2600
Iridium.....	22.4	2350	4800
Iron.....	7.86	1530	3000
Lead.....	11.34	327	1620
Lithium.....	0.534	186	1200
Magnesium.....	1.74	651	1120
Manganese.....	7.2	1260	1900
Mercury.....	13.6	-38.8	357
Molybdenum....	10.2	2620	3700
Nickel.....	8.9	1452	2900
Osmium.....	22.5	2700	5300
Palladium.....	12.0	1555	2200
Platinum.....	21.45	1755	4300
Potassium.....	0.86	62.3	757
Rhodium.....	12.44	1955	2500
Ruthenium.....	12.3	2450	2700
Silver.....	10.5	960.5	1950
Sodium.....	0.97	97.5	878
Strontium.....	2.54	800	1150
Tantalum.....	16.6	2770	4100
Thallium.....	11.8	303.5	1650
Tin.....	7.3	232	2260
Thorium.....	11.2	1845	3000
Titanium.....	4.5	1800	3000
Tungsten.....	19.2	3400	5900
Uranium.....	18.7	1850	—
Vanadium.....	5.9	1710	3000
Zinc.....	7.14	419	907
Zirconium.....	6.4	1700	2900

VII. WEIGHT IN GRAMS OF ONE LITER OF CERTAIN GASES UNDER STANDARD CONDITIONS, AND BOILING POINTS OF THE LIQUIDS UNDER PRESSURE OF 760 mm.

Name of Gas	Weight of 1 Liter	B.P. °C.	Name of Gas	Weight of 1 Liter	B.P. °C.
Acetylene.....	1.162	- 84°	Hydrogen Chloride	1.64	- 83°
Air.....	1.293		Hydrogen Sulfide .	1.54	- 61°
Ammonia.....	0.771	- 33°	Methane.....	0.717	-164°
Argon.....	1.781	-186°	Nitric Oxide.....	1.34	-152°
Carbon Dioxide...	1.976	- 79°	Nitrogen.....	1.2507	-195°
Carbon Monoxide.	1.25	-190°	Nitrous Oxide.....	1.98	- 90°
Chlorine.....	3.2	- 34°	Oxygen.....	1.429	-182.5°
Helium.....	0.1782	-268.9°	Sulfur Dioxide.....	2.93	- 8°
Hydrogen.....	0.08987	-252.5°	Water (vapor).....	0.8045	+100°

VIII. SCALE OF HARDNESS

- | | |
|--------------------------|---------------------------------|
| 1. Talc. | 6. Orthoclase (Potash Feldspar) |
| 2. Rock Salt (or Gypsum) | 7. Quartz |
| 3. Calcite. | 8. Topaz. |
| 4. Fluorite. | 9. Corundum. |
| 5. Apatite. | 10. Diamond |

Each mineral in this list will scratch the surface of any one preceding it.

IX. ELECTROCHEMICAL SERIES OF THE ELEMENTS

THE METALS

Cesium
 Rubidium
 Potassium
 Sodium
 Lithium
 Barium
 Strontium
 Calcium
 Magnesium
 Aluminium
 Manganese
 Zinc
 Chromium
 Iron
 Cadmium
 Cobalt
 Nickel
 Tin
 Lead
 HYDROGEN
 Antimony
 Bismuth
 Arsenic
 Copper
 Mercury
 Silver
 Palladium
 Platinum
 Gold
 Iridium
 Rhodium
 Osmium

THE NON-METALS

Silicon
 Carbon
 Boron
 Nitrogen
 Selenium
 Phosphorus
 Sulfur
 Iodine
 Bromine
 Chlorine
 Oxygen
 Fluorine

X. HEAT OF COMBUSTION OF VARIOUS SUBSTANCES PER GRAM

Substance	Burned to	Heat Evolved, calories
Hydrogen	H ₂ O gas	29150
"	H ₂ O liquid	33900
Carbon (amorphous)	CO ₂	8080
Sulphur (rhombic)	SO ₂	2221
Copper	CuO	590
Magnesium	MgO	6000
Alcohol (ethyl)	CO ₂ + H ₂ O liquid	7080
Methane	CO ₂ + H ₂ O liquid	13344
Ethylene	CO ₂ + H ₂ O liquid	12072
Acetylene	CO ₂ + H ₂ O liquid	11923
Benzene (liquid)	CO ₂ + H ₂ O liquid	10030
Starch	CO ₂ + H ₂ O liquid	4228
Cane Sugar	3961
Tallow	9500
Coal (bituminous)	7800
" (anthracite)	8000
Coke	7770
Petroleum	11000

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SOLUBILITIES OF BASES AND SALTS AT 18°¹

	K	Na	Li	Ag	Tl	Ba	Sr	Ca	Mg	Zn	Pb
Cl	32.95 3.9	35.86 5.42	77.79 13.3	0.0316 0.0410	0.3 0.013	37.24 1.7	51.09 3.0	73.19 5.4	55.81 5.1	203.9 9.2	1.49 0.05
Br	65.86 4.6	88.76 6.9	168.7 12.6	0.041 0.065	0.04 0.0215	103.6 2.9	96.52 3.4	143.3 5.2	103.1 4.6	478.2 9.8	0.598 0.02
I	137.5 6.0	177.9 8.1	161.5 8.5	0.063 0.071	0.006 0.0217	201.4 3.8	169.2 3.9	200 4.8	148.2 4.1	419 6.9	0.08 0.02
F	92.56 12.4	4.44 1.06	0.27 0.11	195.4 13.5	72.05 3.0	0.16 0.0292	0.012 0.001	0.0016 0.02	0.0076 0.0214	0.005 0.05	0.07 0.003
NO ₃	30.34 2.6	83.97 7.4	71.43 7.3	213.4 8.4	8.91 0.35	8.74 0.33	66.27 2.7	121.8 5.2	74.31 4.0	117.8 4.7	51.66 1.4
ClO ₃	6.6 0.52	97.16 6.4	313.4 15.3	12.25 0.6	3.69 0.13	35.42 1.1	174.9 4.6	179.3 5.3	126.4 4.7	183.9 5.3	150.6 3.16
BrO ₃	6.38 0.38	36.67 2.2	152.5 8.20	0.59 0.025	0.30 0.009	0.8 0.02	30.0 0.9	85.17 2.3	42.86 1.5	58.43 1.8	1.3 0.03
IO ₃	7.62 0.35	8.33 0.4	80.43 3.84	0.004 0.0214	0.059 0.0216	0.05 0.001	0.25 0.0257	0.25 0.007	6.87 0.26	0.83 0.02	0.002 0.043
OH	142.9 18	116.4 21	12.04 5.0	0.01 0.001	40.04 1.76	3.7 0.22	0.77 0.063	0.17 0.02	0.001 0.02	0.05 0.045	0.01 0.024
SO ₄	11.11 0.62	16.83 1.15	35.64 2.8	0.55 0.020	4.74 0.09	0.023 0.0410	0.011 0.026	0.20 0.015	35.43 2.8	53.12 3.1	0.0041 0.0213
CrO ₄	63.1 2.7	61.21 3.30	111.6 6.5	0.0025 0.0215	0.006 0.021	0.0238 0.0415	0.12 0.006	0.4 0.03	73.0 4.3	0.042 0.065
C ₂ O ₄	30.27 1.6	3.34 0.24	7.22 0.69	0.0035 0.02	1.48 0.030	0.0086 0.0238	0.0046 0.0226	0.0256 0.0443	0.03 0.0027	0.026 0.04	0.0215 0.05
CO ₃	108.0 5.9	19.39 1.8	1.3 0.17	0.003 0.021	4.95 0.10	0.0023 0.0211	0.0011 0.027	0.0013 0.0213	0.1 0.01	0.004? 0.023?	0.021? 0.043

The upper number in each square gives the number of grams of the anhydrous salt held in solution by 100 cc. of water. The lower number is the molar solubility, *i.e.*, the number of *moles* of the salt contained in one liter of the saturated solution.

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PERIODIC TABLE*

Periods	Group 0	Group I	Group II	Group III	Group IV	Group V	Group VI	Group VII	Group VIII
Type of Oxide	—	RO RH	RO RH ₂	R ₂ O ₃ RH ₃	RO ₂ RH ₄	R ₂ O ₅ RH ₅	R ₂ O ₅ (RO ₂) RH ₆	R ₂ O ₇ RH	RO ₄ —
Type of Hydride.....	—	A H ₁ Li 3 1.008 B 6.94	A B	A B	A B	A B	A B	A B	—
First short period.....	He 2 4.002		Be 4 9.02	B 5 10.82	C 6 12.00	N 7 14.01	O 8 16.00	F 9 19.0	
Second short period.....	Ne 10 20.183	Na 11 23	Mg 12 24.32	Al 13 26.97	Si 14 28.06	P 15 31.03	S 16 32.06	Cl 17 35.46	
First long period	A 18 39.94	K 19 39.1 Cu 29 63.57	Ca 20 40.07 Zn 30 65.38	Sc 21 45.1 Ca 31 69.72	Ti 22 47.9 Ce 32 72.6	V 23 50.96 As 33 74.96	Cr 24 52.01 Se 34 79.2	Mn 25 54.93 Br 35 79.92	Fe 26 Co 27 Ni 28 55.84 58.94 58.69
Second long period	Kr 36 82.9	Rb 37 85.44 Ag 47 107.88	Sr 38 87.63 Cd 48 112.41	Y 39 88.92 In 49 114.8	Zr 40 91.22 Sn 50 118.7	Cb 41 93.1 Sb 51 121.77	Mo 42 96.0 Te 52 127.5	Ma 43 ? I 53 126.93	Ru 44 Rh 45 Pd 46 101.7 102.91 106.7
Third long period	Xe 54 130.2	Cs 55 132.81	Ba 56 137.37	La 57 138.9	Ce 58 140.25				
The Rare Earth Elements. Atomic Numbers 59-71									
Fourth long period		Au 79 197.2	Hg 80 200.61	Tl 81 204.39	Hf 72 178.6 Pb 82 207.22	Ta 73 181.5 Bi 83 209.0	W 74 184.0 Po 84 ?	Re 75 ?	Os 76 Ir 77 Pt 78 190.8 193.1 195.23
Fifth period.....	Rn 86 222	—87	Ra 88 226.95	Ac 89	Th 90 232.15	U 91 238.17			

* The number at the right of the symbol is the Atomic Number of the element, and the number below is the Atomic Weight.

